FINAL REPORT

Wash Primer Replacement based on the Superprimer Technology

SERDP Project WP-1675

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14. ABSTRACT
A replacement for the wash primer that meets the military specification DoD-P-15328D has been developed. It is water-borne, contains no hexavalent chromium, has very low VOC and contains no HAPs. It has been tested on cold-rolled steel and the aluminum alloy AA7075-T6. On both metals the proposed replacement exceeds the performance of the DoD-P-15328D primers in various tests, including SST, EIS and CCT. Adhesion to primers is also improved by the new wash primer. The application process is simple and the metal pretreatment is not critical.

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List of Acronyms

AA =	Aluminum Alloy
AFM =	Atomic Force Microscopy
ASTM =	American Society for Testing Materials
BLK =	Blank (control)
CARC =	Chemical-Agent-Resistant Coating
CASS =	Copper-Accelerated Salt Spray (Test)
CCT =	Cyclic Corrosion Testing
CRS =	Cold-Rolled Steel
CW =	City Water
DIW =	Deionized Water
DTM =	Direct-to-Metal (Coating)
EDTA =	Ethylene Diamine Tetra Acetic Acid
EDX =	Energy-Dispersive X-ray (Spectroscopy)
EGS =	Electrogalvanized Steel
EIS =	Electrochemical Impedance Spectroscopy
EPA =	Environmental Protection Agency
ESEM =	Environmental Scanning Electron Microscopy
ESTCP =	Environmental Security Technology Certification Program
FTIR =	Fourier-Transform Infrared Spectroscopy
GM =	General Motors
HAP =	Hazardous Air Pollutant
HDG =	Hot-Dip Galvanized Steel
HVLP =	High-Volume Low-Pressure
NSF =	National Science Foundation
PU =	Polyurethane
PVB =	PolyVinyl Butyral
RH =	Relative Humidity

RT = Room Temperature

SB = Solvent-Borne

SBIR = Small Business Innovation Research

SERDP = Strategic Environmental Research and Development Program

SP = Superprimer

SST = Salt Spray Testing

UC = University of Cincinnati

VOC = Volatile Organic Compound

WB = Water-Borne

WP = Wash Primer

ZP = Zinc Phosphate

Key Words

wash primer, silanes, corrosion, protection, paint, primer, adhesion, metals, pretreatment, steel, aluminum

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Personnel at the Army Research Laboratories are acknowledged for their interest in this project and their valuable advice on materials and test conditions.

Wash Primer Replacement based on the Superprimer Technology

Abstract

Objective

The objective was to obtain a new wash primer formulation that performs well on primarily CRS and also on aluminum alloys, that is completely devoid of Cr(VI), HAPs, phosphoric acid and has low VOC, without sacrificing corrosion protection performance under typical water-borne and solvent-borne primers and topcoats. Part of the objective was also that the replacement primer can be used without requiring a change to the existing infrastructure, i.e., it should be a drop-in process.

Technical Approach

The superprimer (SP) technology, developed in an earlier SERDP project [1], was selected as a basis from which a new wash primer could be developed. SPs are mixtures of silanes, water-dispersed resins, anti-corrosion pigments and other ingredients. They can be applied on bare substrates by means of dipping, brushing, spraying or rolling. They do not require a metal pretreatment such as a conversion coating (phosphate or chromate). Their adhesion to metallic substrates is good, due to the presence of the silane in the coating. Their adhesion to a primer or topcoat can also be good. They do not contain Cr(VI) pigments for corrosion protection of the metal substrate. Thus, the proposed project focused on the reduction of the 25 μm SP to a 8-10 μm wash primer with equal performance.

Results

A number of systems that perform well on the substrates cold-rolled steel (CRS) and aluminum alloy AA7075 (AA) have been developed. The preferred system is water-borne and consists of a metal compound, a prehydrolyzed silane and a water-dispersed epoxy resin. It forms a film that is considerably thinner than 8 μm, is stable over a long period of time, contains zero VOC, zero HAP and no chromate. It performs well under water-borne and solvent-borne military primers and can rival the performance of the wash primers that meet the DoD-P-15328D specifications on CRS. On AA the performance exceeds the DoD-P-15328D specifications, because the new wash primer etches both CRS and AA, while the DoD-P-15328D wash primers can etch CRS but not AA.

The test protocols used in this project were:

1. ASTM B-117 salt spray test; scribed; primed only
2. GM9540P cyclic corrosion test (CCT); scribed; primed only
3. Electrochemical Impedance Spectroscopy (EIS) of panels exposed in the CCT test; not scribed; primed only

4. Exposure at the Battelle subtropical exposure site in Florida; not scribed; topcoated; still in progress
6. Copper-Accelerated Acid Salt Spray Test (CASS, ASTM B368); for AA; scribed; primed only; in progress
7. Humidity Test (ASTM 2247); not scribed; primed only; in progress

Benefits

The new wash primer can be applied as a drop-in technology by spraying, dries quickly at room temperature, has very low VOC, provides good adhesion and corrosion resistance and is devoid of chromate. It can be used on several different metals such as CRS and AA7075-T6. It is a one-pack system which is stable for months. It can be applied with conventional painting equipment in conventional paint booths. It works well under several different primers, whether water-borne or solvent-borne. A new water-borne primer with improved properties over water-borne primers that meets the MIL-P-53030C specifications is also available. The new wash primer works very effectively with that primer.

Section 1. Evaluation and Optimization of the UC Superprimers as Replacements of DoD-P-15328D Wash Primers

1.1. Background

The superprimer technology was developed at the University of Cincinnati in a previous SERDP project [1]. In this project, two environmentally friendly coating systems were formulated for metallic structural components in DoD systems. These two novel waterborne coating systems (or superprimers), were, (1) a 2-K epoxy-acrylate-silane superprimer (**UC-1**) and, (2) a 2-K novolac-polyurethane-silane superprimer (**UC-2**). It has been successfully demonstrated that both UC-1 and UC-2 can provide excellent corrosion resistance to metal substrates, such as AA2024-T3, even without using conventional metal pretreatments [1].

The superprimers typically comprise the following components: (1) bis-silanes or their mixtures, (2) water-dispersible organic resins, (3) chromate-free anti-corrosion pigments and, (4) other additives. They can be applied on bare substrates by means of dipping, brushing, spraying or rolling, i.e., all possible industrial application methods. However, these two superprimers do not require any prior conversion coatings such as a phosphating or chromating. Their solid content is about 30-40%, and the typical coating thickness of both superprimers is 25 μm.

Because of their past success, UC-1 and UC-2 were initially evaluated on different metal substrates under military primers in this project. Optimization work was also done for UC-1 and UC-2 in an attempt to narrow the performance gap between the superprimers and DoD-P-15328D primers. The following section reports the details of these experiments.

1.2. Materials and Methods

Metal substrates: Three main substrates used here included cold-rolled steel (CRS), hot-dipped galvanized steel (HDG G70) and aluminum alloy AA6061-T6. All test panels were purchased from ACT Test Panels Inc.

UC superprimer formulas and their modified versions: The formulas of UC-1 and UC-2 and their modified versions are shown in Tables 1 and 2. Prior to coating application, these formulations were further diluted to around 16% solid content so that the resultant primer thickness could be controlled to between 7-12 μm.

Military primers: Three military primers were used for the evaluation of superprimers on the metal substrates. These military primers were: (1) MIL-PRF-23377J (chromate-containing, solvent-borne epoxy polyamide primer, Type 1, Class C2, VOC = 450 g/l); (2) MIL-PRF-85582D (chromate-containing, water-borne epoxy polyamide primer, Type 1, Class C2) and, (3) MIL-DTL-53030B (chomate-free, waterborne epoxy polyamide primer). Primers meetings these military specs were manufactured by NCP Coatings Inc. and were purchased from their distributor D&S Color Supply, Inc.

Surface treatment and coating procedures: these were as follows:
Alkaline cleaning; city water rinse; DI water rinse; hot-air drying (30 s); spraying with wash primer candidates (conventional HVLP spray, 30 psi); drying at ambient for at least 30 min.; epoxy primer spraying; curing for 2 weeks at ambient conditions.

The dried wash primer thickness was controlled at 8-12 μm, and the cured epoxy primer thickness was controlled at 25-35 μm.

Table 1. Formulas of Epoxy-Acrylic superprimer (UC-1) (in wt.%)

Part A	UC-1	UC-1B	UC-1S1	UC-1S2	UC-1S3	UC-1S4
Zinc phosphate[1]	27	27	27	27	27	27
Silquest A-1289[2]	3	0	3	3	3	3
Maincote AE-58[3]	52	52	52	52	52	52
Surfynol 104H[4]	1	1	1	1	1	1
Part B						
Daubond DC 9010[5]	6	6	6	6	6	6
Butyl Cellosolve[6]	5	5	5	5	5	5
15% $NaNO_3$	1	1	1	1	1	1
DI water	4	4	4	4	4	4
BTSE[7]		3				
Cab-O-Sil TS 720[8]			1			
Cab-O-Sil AFS[9]				1		
Aerosil OX 50[10]					1	
Aerosil 200[11]						1

1. Anticorrosion pigment, from Molywhite, Inc.
2. Bis-triethoxysilylpropyl polysulfide, from Momentive Performance, Inc.
3. Acrylic emulsion, from Rohm & Haas Co.
4. Wetting agent, from Air Products Co.
5. Epoxy water dispersion, from Daubert, Inc.
6. 2-Butoxyethanol, from Dow Chemicals
7. Bis-1,2-(triethoxysilyl) ethane, from Momentive Performance Inc.
8. Treated fumed silica, a rheology modifier, from Cabot Co.
9. Treated fumed silica, a rheology modifier, from Cabot Co.
10. Fumed silica, from Evonik Industries
11. Fumed silica, from Evonik Industries

Table 2. Formulas of Novolac-Polyurethane superprimer (UC-2) (in wt.%)

Part A	UC-2	UC-2B	UC-2S1	UC-2S2	UC-2S3	UC-2S4
Zinc phosphate[1]	22	22	22	22	22	22
DI water	13	13	13	13	13	13
DPC 6870[2]	12	12	11	11	11	11
Part B						
Novolac 5003[3]	46	46	46	46	46	46
A1289[4]	3		3	3	3	3
NEO REZ-R972[5]	4	4	4	4	4	4

BTSE[6]		3				
Cab-O-Sil TS 720[7]			1			
Cab-O-Sil AFS[8]				1		
Aerosil OX 50[9]					1	
Aerosil 200[10]						1

1. Anticorrosion pigment, from Molywhite Inc.
2. Epoxy curing agent, from Hexion
3. Novolac epoxy dispersion, from Hexion
4. Bis-triethoxysilylpropyl polysulfide, from Momentive Performance Inc.
5. Polyurethane dispersion, from DSM Co.
6. Bis-1,2-(triethoxysilyl) ethane, from Momentive Performance Inc.
7. Treated fumed silica, an efficient rheology modifier, from Cabot Co.
8. Treated fumed silica, an efficient rheology modifier, from Cabot Co.
9. Fumed silica, from Evonik Industries
10. Fumed silica, from Evonik Industries

Test methods: The following performance tests were conducted in this section of the project.

1. **Neutral salt spray test (ASTM B117):** to evaluate the corrosion resistance of the coated metal substrates in a corrosive environment; this is a continuous salt fog spray with 5% NaCl solution (pH 6.5); the testing temperature was 35°C and the humidity was 100% Rh.

2. Adhesion test (ASTM D 3359): both dry and wet adhesion performance of the coated metal substrates were evaluated. The dry paint adhesion test was immediately conducted after the paints were fully cured, while the wet paint adhesion was determined after the painted metal substrates were immersed in DI water for 24 hrs in ambient conditions.

1.3. Test results and discussion

1.3.1. Paint adhesion test results

Table 3 displays the paint adhesion performance of the diluted UC-1 and UC-2 superprimers on different metals under the MIL-PRF-23377J primer. Both UC-1 and UC-2 performed well on CRS and HDG but UC-1 did not perform on AA 6061where no paint adhesion was obtained at all (0B). The control DoD-P-15328D performed well on the three metal substrates, showing no paint loss (5B).

Table 3. Paint adhesion of diluted superprimers under MIL-PRF-23377J

ID	CRS		HDG		AA6061	
	Dry	Wet	Dry	Wet	Dry	Wet
UC-1	5B	5B	5B	5B	0B	0B
UC-2	5B	5B	5B	5B	4B	4B
DoD-P-15328D	5B	5B	5B	5B	5B	5B

Table 4 displays the paint adhesion performance of the diluted UC-1 and UC-2 superprimers on different metals under the MIL-PRF-85582D primer. Both UC-1 and UC-2 performed

reasonably well on CRS and HDG but again UC-1 failed on AA6061where no paint adhesion was obtained (0B). This result is similar to that under MIL-PRF-23377J. Unlike under MIL-PRF-23377J, DoD-P-15328D behaves poorly here on HDG and AA6061 where no paint adhesion was obtained (0B).

Table 4. Paint adhesion of diluted superprimers under MIL-PRF-85582

ID	CRS		HDG		AA6061	
	Dry	Wet	Dry	Wet	Dry	Wet
UC-1	5B	4B	3B	3B	0B	0B
UC-2	4B	4B	4B	4B	5B	4B
DoD-P-15328D	4B	4B	0B	0B	0B	0B

Table 5 shows the paint adhesion results for the diluted UC-1 and UC-2 superprimers on the metals under the MIL-DTL-53030B primer. In this case, none of the tested wash primers can provide decent paint adhesion to this chromate-free, water-borne epoxy primer on any of the metal substrates. This may indicate that the quality of MIL-DTL-53030B is inferior to that of the MIL-PRF-23377J and MIL-PRF-85582 primers.

Table 5. Paint adhesion of diluted superprimers under MIL-DTL-53030B

ID	CRS		HDG		AA6061	
	Dry	Wet	Dry	Wet	Dry	Wet
UC-1	3B	1B	2B	1B	0B	0B
UC-2	2B	0B	2B	1B	3B	1B
DoD-P-15328D	4B	1B	4B	2B	4B	2B

The paint adhesion data can be summarized a follows.

- Diluted superprimers UC-1 and UC-2 can provide good paint adhesion for CRS, AA6061 and HDG under the chromate-containing, solvent-borne epoxy primers (MIL-PRF-23377J), but they do not perform satisfactorily under the two waterborne epoxy primers MIL-PRF-85582 and MIL-DTL-53030B.
- MIL-DTL-53030B seems to have a poorer quality than the SB MIL-PRF-23377J and MIL-PRF-85582 primers, in which strontium chromate is used as the major corrosion inhibitor. The MIL-DTL-53030B primer contains zinc phosphate as corrosion inhibitor. None of the tested wash primers, including DoD-P-15328D, adheres well to this primer.
- The diluted UC-1 and UC-2 as well as DoD-P-15328D perform best on CRS, but are less effective on HDG and AA6061. In the case of MIL-PRF-85582, DoD-P-15328D performed poorly on HDG and the AA alloy. A possible cause for this unexpected performance could be that both HDG and AA 6061 were cleaned with a silicate-containing alkaline cleaner. The silicate residues on the HDG and AA6061 panels may adversely affect the adhesion between the wash primers and the metal substrates.

In an attempt to improve the paint adhesion performance for MIL-DTL-53030B, UC-1 and UC-2 were modified by varying silane types and adding nano-scaled silica particles. The modified formulas were also given in Tables 1 and 2. Tables 6 and 7 display the paint adhesion test results for these modified UC-1 and UC-2 superprimers under the MIL-DTL-53030B primer. It is seen in the tables that the dry adhesion performance of both UC-1 and UC-2 was significantly improved for CRS but not for HDG and AA6061. The wet adhesion performance for all the metals under MIL-DTL-53030B was not improved significantly.

Table 6. Paint adhesion of modified UC-1 superprimers under MIL-DTL-53030B

ID	CRS		HDG		AA 6061	
	Dry	Wet	Dry	Wet	Dry	Wet
UC-1	3B	1B	2B	1B	0B	0B
UC-1B	4B	2B	4B	2B	0B	0B
UC-1S-1	5B	0B	NA	NA	1B	0B
UC-1S-2	5B	2B	NA	NA	1B	0B
UC-1S-3	5B	0B	NA	NA	0B	0B
UC-1S-4	5B	0B	NA	NA	2B	0B
DoD-P-15328D	4B	1B	4B	2B	4B	2B

Table 7. Paint adhesion of modified UC-2 superprimers under MIL-DTL-53030B

ID	CRS		HDG		AA 6061	
	Dry	Wet	Dry	Wet	Dry	Wet
UC-2	2B	1B	2B	1B	3B	1B
UC-2B	5B	0B	4B	2B	4B	2B
UC-2S-1	2B	1B	N/A	N/A	4B	0B
UC-2S-2	4B	0B	N/A	N/A	4B	0B
UC-2S-3	4B	0B	N/A	N/A	5B	0B
UC-2S-4	4B	1B	N/A	N/A	5B	0B
DoD-P-15328D	4B	1B	4B	2B	4B	2B

1.3.2. Salt spray test results

The corrosion-protection performance of the diluted UC-1 and UC-2 superprimers was evaluated in the standard salt spray test under the military epoxy primers. The test results are reported in mm creepage from the scribe (one-sided) and are given in Tables 8 through 10. Clearly, neither UC-1 nor UC-2 performs as well as DoD-P-15328D in this test. In the case of MIL-DTL-53030B (Table 10), even DoD-P-15328D loses its good performance after 250 hrs in the test, again indicating that MIL-DTL-53030B may be a poor primer not only in adhesion, but also in its protective performance. It is suspected that this primer is rather hydrophilic, resulting in a higher rate of electrolyte diffusion though the paint film than in the case of the other two.

Table 8. Salt spray test results (mm creep) for the superprimers under MIL-PRF-23377J

ID	CRS		HDG		AA6061	
	250 (hr)	1000 (hr)	250 (hr)	1000 (hr)	250 (hr)	1000 (hr)
UC-1	2.0	CD*	0.5	CD	0.0	CD
UC-2	CD	CD	0.5	CD	0.0	LD**
DoD-P-15328D	0.5	0.5	0.0	0.5	0.0	0.0

*CD = complete delamination; **LD = large delamination

Table 9. Salt spray test results (mm creep) for the superprimers under MIL-PRF-85582D

ID	CRS		HDG		AA6061	
	250 (hr)	1000 (hr)	250 (hr)	1000 (hr)	250 (hr)	1000 (hr)
UC-1	CD*	CD	0.5	LD**	2.0	CD
UC-2	2.5	CD	0.5	CD	1.0	5.0
DoD-P-15328D	0.5	2.0	0.5	4.0	1.0	3.0

*CD = complete delamination; **LD = large delamination

Table 10. Salt spray test results for the superprimers under MIL-PRF-53030B

ID	CRS		HDG		AA6061	
	250 (hr)	1000 (hr)	250 (hr)	1000 (hr)	250 (hr)	1000 (hr)
UC-1	LD	NA	2.0	NA	CD	NA
UC-2	CD	NA	1.0	NA	2.0	NA
DoD-P-15328D	1.0	NA	0.0	NA	0.0	NA

*CD = complete delamination; **LD = large delamination

Tables 11 and 12 show the test results for the modified UC-1 and UC-2 primers under MIL-DTL-53030B. Apparently, the modifications did not lead to a significant improvement in term of the corrosion protection performance, which is poor as compared to that of DoD-P-15328D.

Table 11. Salt spray test results for the modified UC-1 under MIL-DTL-53030B primer

ID	CRS (72 hrs)	HDG (250 hrs)	AA6061 (250 hrs)
UC-1	LD	3.0	CD
UC-1B	CD*	2.5	CD
UC-1S-1	LD**	N/A	4.0
UC-1S-2	LD	N/A	2.0
UC-1S-3	LD	N/A	CD
UC-1S-4	LD	N/A	7.0
DoD-P-15328D	0.0	0.0	0.0

*CD = complete delamination; **LD = large delamination

Table 12. Salt spray test results for the modified UC-2 under MIL-DTL-53030B primer

ID	CRS (72 hrs)	HDG (250 hrs)	AA6061 (250 hrs)
UC-2	2.0	4.0	2.0
UC-2B	CD*	1.5	3.0
UC-2S-1	CD	N/A	LD
UC-2S-2	CD	N/A	1.5
UC-2S-3	CD	N/A	1.0
UC-2S-4	CD	N/A	1.0
DoD-P-15328D	0.0	0.0	0.0

*CD = complete delamination

1.4. Summary of Section 1

The diluted UC-1 and UC-2 superprimers and several modified versions of them were evaluated on CRS, AA6061 and HDG under military epoxy primers in both paint adhesion and accelerated corrosion tests. The following conclusions can be drawn.

- The superprimers UC-1 and UC-2, previously developed at the University of Cincinnati, can be diluted to lower solid content, i.e., 16-20%, with DI water, and can then be readily sprayed on metal substrates using a conventional HVLP spray gun. The resulting dry coating thickness was 7-12 μm, similar to that of DoD-P-15328D.
- The diluted UC-1 and UC-2 provide excellent dry and wet paint adhesion under MIL-PRF-23377J (solvent-borne, chromate-containing epoxy primer) on all metal substrates (CRS, AA6061 and HDG), similar to DoD-P-15328D. Both diluted superprimers, however, failed under the two waterborne epoxy primers MIL-PRF-85582 and MIL-DTL-53030B. It is also noted that DoD-P-15328D did not perform satisfactorily under MIL-DTL-53030B, the water-borne, chromate-free epoxy primer.
- A formula modification of UC-1 and UC-2 noticeably improved their dry paint adhesion under the MIL-DTL-53030B primer, but no positive effect was obtained for the wet adhesion performance.
- In the salt spray test, neither UC-1 nor UC-2 or their modified versions could deliver the good anti-corrosive performance under the three military primers that was observed for the DoD-P-15328D wash primer.
- In this Section 1 it was observed that a silicate-based alkaline cleaner used for metal panels cleaning possibly adversely affected the performance of all tested wash primers including DoD-P-15328D on AA6061 and HDG. It is conceivable that the silicate residue on AA6061 and HDG somehow hindered the interaction of the wash primers and the metals, for instance the etching effect of the phosphoric acid could have been impaired. Such influence on CRS seems to be absent, as silicate does not precipitate on this metal.
- The above test results indicated that the diluted superprimers could not deliver sufficient corrosion protection on metals under the military epoxy primers that were used. Hence,

further development of such primers was abandoned and the main focus of the next stage would be to find an effective formula from scratch that would be able to provide equal or better corrosion protective performance than that of DoD-P-15328D wash primers. It should be noted that the basic underlying idea, viz., using a water-borne chromate-free superprimer (i.e., water-dispersed resins with silanes) was not given up but maintained in the remainder of the project.

Section 2. Evaluation and Optimization of ECOSIL Superprimers as Replacements for DoD-P-15328D Wash Primers

2.1. Background

The UC superprimers developed in an earlier SERDP project and their revised versions were evaluated as starting formulas in this project and were compared with a DoD-P-15328D wash primer. The test results indicated that in dilute form these superprimers were not capable of replacing the DoD-P-15328D primer. Two ECOSIL water-borne primers were then considered as candidate replacement and were further evaluated and optimized in this section. These two primers were, (1) a 2-K water-borne epoxy-silane primer (**E-11**), and, (2) a 1-K acrylic-polyurethane-silane primer (**AU-23**). E-11 had been developed by ECOSIL in an SBIR Phase I project.

E-11 is a 2-K water-borne epoxy primer, which is cured at RT with a polyamine. Advanced silane chemistry is used in the development of E-11 system for further performance enhancement. The VOC content of E-11 is very low, i.e., about 50 g/L. The solid content of E-11 is 33%. E-11 has demonstrated excellent anti-corrosion performance as a DTM (direct-to-metal) coating on multiple metals such as AA6061 and HDG. DTM means that the coating can be used on metals without the use of a pretreatment such as chromating or phosphating. The coating thickness is variable. The primer has been used successfully at ECOSIL in the thickness range of 25-100 μm. Therefore, for the purpose of using it as a wash primer it had to be modified so that it would still perform at lower thickness.

AU-23 is a 1-K waterborne acrylic-polyurethane-based primer. It was initially designed to function as an organic thin film on galvanized steels such as HDG and EGS. The solid content of AU-23 is 13-16%. It contains no VOCs or HAPs. AU-23 applied as a thin organic film (<2 μm) has achieved 96 hrs performance (<5% white rust) on EGS and 120 hrs on HDG in a salt spray test (ASTM B117).

In this stage, two additional solvent-borne formulas, labeled EPZ-0 and EPZ-1, were developed from scratch as well and compared with the DoD-P-15328D wash primer. In this section the results obtained with these four potential wash primer replacements are presented.

2.2. Materials and Methods

Metal substrates: The metal substrate used in this section here was cold-rolled steel (CRS), purchased from ACT Test Panels Inc.

Formulas and their modified versions: The formulas for EPZ-0 and EPZ-1 are listed in Table 13. Table 14 shows the modification details for the AU-23 formula. The additives tested in AU-23 included various anti-corrosion inhibitors and surfactants.

Military primers and topcoats: The military primers used were, (1) MIL-PRF-23377J (chromate-containing, solvent-borne epoxy polyamide primer, Type 1, Class C2, VOC = 450 g/L) and, (2) MIL-P-53022C (chromate-free, solvent-borne 2-K epoxy-polyamide primer). A CARC topcoat was also used here. It was MIL-C-53039A (black moisture-cured CARC camouflage topcoat, polyurethane-based.). These military primers and topcoat were manufactured by NCP Coatings Inc. and were purchased from their distributor, D&S Color Supply, Inc.

Table 13. Formulas of EPZ-0 and EPZ-1 (in wt.%)

Component	EPZ-0	EPZ-1
Beckopox® EM 460[1]	17.6	17.5
PVB (Mowital B 30 H)[2]	10.8	10.88
Zinc phosphate[3]	0	0.3
H_3PO_4/Butanol (1:3)	4.1	4.0
Butyl Cellosolve[4]	67.6	67.3

1. Epoxy resin from Cytec Industries, Inc.
2. Polyvinyl butyral, 100%, from Kuraray America, Inc.
3. Anticorrosion pigment from Molywhite, Inc.
4. 2-Butoxyethanol from Dow Chemicals

Table 14. Modified AU-23 formulas (in wt.%)

Component	AU-23(A)	AU-23(B)	AU-23(C)	AU-23(D)	AU-23(E)	AU-23(F)
AU-23	99.5	99.9	99.0	98.5	99.0	99.0
SA-PO[1]	0.5	0.1		0.5		0.5
Thirourea[2]			1.0		0.5	0.5
EDTA[3]				1	0.5	

1. Anti-corrosion pigment developed by ECOSIL in an NSF-funded project
2. Corrosion inhibitor from Sigma Aldrich Co.
3. Corrosion inhibitor from Sigma Aldrich Co.

Surface treatment and coating procedures were as follows:

Alkaline cleaning; city water rinse; DI-water rinse; hot-air drying (30 s); spraying with wash primer candidates (conventional HVLP spray, 30 psi; ambient drying (at least 30 min.); epoxy primer spraying; curing at ambient; topcoating; curing for at least 2 weeks at ambient.

The dried E-11 primer thickness was controlled at 7-12 μm, while the AU-23 thickness was around 5 μm. The cured epoxy primer thickness was controlled at 25-35 μm. The cured topcoat thickness was 50 to 75 μm.

Test methods: The following performance tests were conducted in this section.

1) Neutral salt spray test (SST, ASTM B117): to evaluate the corrosion resistance of the coated metal substrates in a corrosive environment. The test consisted of a continuous salt fog spray

with 5% NaCl solution of pH = 6.5; the test temperature was 35°C and the humidity was 100% RH. The scribe creep was measured in mm (one-sided).

2) Cyclic corrosion test (CCT, GM 9540P): this is another accelerated corrosion test of coated metal substrates. This test is used in automotive industry and its result is believed to correlate to outdoor exposure test results more accurately than those generated in the salt spray test. It is a cyclic test which includes dry-out steps.

3) Adhesion test (ASTM D 3359): both dry and wet adhesion performance of the coated metal substrates were evaluated. The dry paint adhesion was immediately conducted after the paints were fully cured, while the wet paint adhesion was evaluated after the painted metal substrates had been immersed in DI water for 72 hrs at ambient conditions.

4) Impact resistance test (ASTM D2794): the coating flexibility and adhesion under very rapid deformation is evaluated in this test. The load forces used were: 20, 40, 80 and 160 in-lb.

2.3. Test results and discussion

2.3.1. Paint adhesion and impact resistance test results

Paint adhesion and impact resistance tests were conducted for E-11 and AU-23 as candidate wash primers on CRS under two military primers and a CARC topcoat, i.e., MIL-PRF-23377J/MIL-C-53039A and MIL-P-53022C/MIL-C-53039A, respectively. The test results are presented in Table 15. All wash primers exhibited excellent dry and wet paint adhesion, with the ranking of 4B and above. In the impact resistance test, E11 was the best performer and outperformed AU-23 and the DoD-P-15328D wash primer.

AU-23 was further modified by adding corrosion inhibitors. Table 16 presents the test results for these modified AU-23 formulations on CRS under the two military coating systems. No significant improvement of the impact resistance was obtained with these modifications.

Table 17 displays the test results for the two solvent-borne wash primers EPZ-0 and EPZ-1, developed in this SERDP project from scratch. Their formulas are listed in Table 13. Similar results are obtained for EPZ-0 and EPZ-1 under the two military coating systems, i.e., very good paint adhesion but poor impact resistance (< 20 lb-in).

Table 15. Paint adhesion and impact resistance for E-11 and AU-23 on CRS under epoxy primers and a CARC topcoat

Sample ID	MIL-PRF-23377J/MIL-C-53039A			MIL-P-53022C/MIL-C-53039A		
	Dry adhesion	Wet adhesion	Impact (lb-in)	Dry adhesion	Wet adhesion	Impact (lb-in)
E11	4B	4B	160	5B	5B	160
AU-23	5B	5B	< 20	4B	5B	< 20
DoD-P-15328D	5B	5B	40	5B	5B	40

Table 16. Paint adhesion and impact resistance for modified AU-23 formulations on CRS under epoxy primers and a CARC topcoat

Sample ID	MIL-PRF-23377J/MIL-C-53039A			MIL-P-53022C/MIL-C-53039A		
	Dry adhesion	Wet adhesion	Impact (lb-in)	Dry adhesion	Wet adhesion	Impact (lb-in)
AU-23	5B	5B	< 20	4B	5B	< 20
AU-23(A)	5B	5B	< 40	5B	4B	< 40
AU-23(B)	5B	5B	< 40	5B	4B	< 40
AU-23(C)	4B	4B	40	5B	0B	< 40
AU-23(D)	5B	5B	40	4B	0B	< 40
AU-23(E)	5B	5B	< 40	4B	0B	< 40
AU-23(F)	5B	5B	< 40	4B	3B	< 40
DoD-P-15328D	5B	5B	40	5B	5B	40

Table 17. Paint adhesion and impact resistance for solvent-borne EPZ-0 and EPZ-1 formulations on CRS under epoxy primers and a CARC topcoat

Sample ID	MIL-PRF-23377J/MIL-C-53039A			MIL-P-53022C/MIL-C-53039A		
	Dry adhesion	Wet adhesion	Impact (lb-in)	Dry adhesion	Wet adhesion	Impact (lb-in)
EPZ-0	4B	4B	< 20	4B	4B	< 20
EPZ-1	5B	5B	< 20	5B	5B	< 20
DoD-P-15328D	5B	5B	40	5B	5B	40

2.3.2. Accelerated corrosion test results

E-11, AU-23, modified AU-23, EPZ-0 and EPZ-1 were further evaluated in two accelerated corrosion tests, viz., the neutral salt spray test (ASTM B117) and the cyclic corrosion test (GM 9540P). E-11 failed in both tests, but AU-23's performance was similar to that of DoD-P-15328D in SST after 168 hrs and in CCT after 20 cycles, as shown in Table18.

Table 18. SST and CCT results for E-11 on CRS under military primers and a CARC topcoat (creep in mm from the scribe)

Sample ID	MIL-PRF-23377J/MIL-C-53039A		MIL-P-53022C/MIL-C-53039A	
	SST (168 hrs)	GM 9540P (20 cycles)	SST (168 hrs)	GM9540P (20 cycles)
E-11	LD*	>10	LD	>10
AU-23	0	1.5	0	1.5
DoD-P-15328D	0	0	0	0

*LD = Large Delamination

Further AU-23 modification did not lead to better performance in prolonged test periods in both SST and CCT, i.e., >336 hrs in SST and 40 cycles in CCT. The test results for modified AU-23

formulations are presented in Table 19. AU-23(A) and AU-23(B) performed the best among all the modified formulations. Still, they cannot meet the performance level of DoD-P-15328D after 500 hrs of SST and 40 cycles of CCT.

Table 19. SST and CCT results for AU-23 and modified versions on CRS under epoxy primers and a CARC topcoat (creep in mm from the scribe)

Sample ID	MIL-PRF-23377J/MIL-C-53039A			MIL-P-53022C/MIL-C-53039A		
	SST (336 hrs)	SST (500 hrs)	GM 9540P (40 cycles)	SST (336 hrs)	SST (500 hrs)	GM 9540P (40 cycles)
AU-23(A)	1.5	5	5.5	1	5.5	5
AU-23(B)	2	6	7	1.5	7	8
AU-23(C)	LD*	N/A	>10	LD	N/A	>10
AU-23(D)	3.5	N/A	>10	3.5	N/A	>10
AU-23(E)	LD	N/A	>10	LD	N/A	>10
AU-23(F)	LD	N/A	>10	LD	N/A	>10
DoD-P-15328D	0.5	1	5	0.5	1	6

*LD = Large Delamination

Table 20 shows the test results for solvent-borne EPZ-0 and EPZ-1 under two military coating systems. Only SST was conducted here. After 336 hrs of exposure, both EPZ-0 and EPZ-1 performed as well as the DoD-P-15328D wash primer, with an average creep of 1 mm from the scribe. After 500 hrs, however, the performance of EPZ-0 and EPZ-1 had become worse than that of the DoD-P-15328D wash primer.

Table 20. SST and CCT results for EPZ-0 and EPZ-1 on CRS under epoxy primers and a CARC topcoat (creep in mm from the scribe)

Sample ID	MIL-PRF-23377J/MIL-C-53039A		MIL-P-53022C/MIL-C-53039A	
	SST (336 hrs)	SST (500 hrs)	SST (336 hrs)	SST (500 hrs)
EPZ-0	1	3	1	4
EPZ-1	1	3	1	5
DoD-P-15328D	1	2	1	2

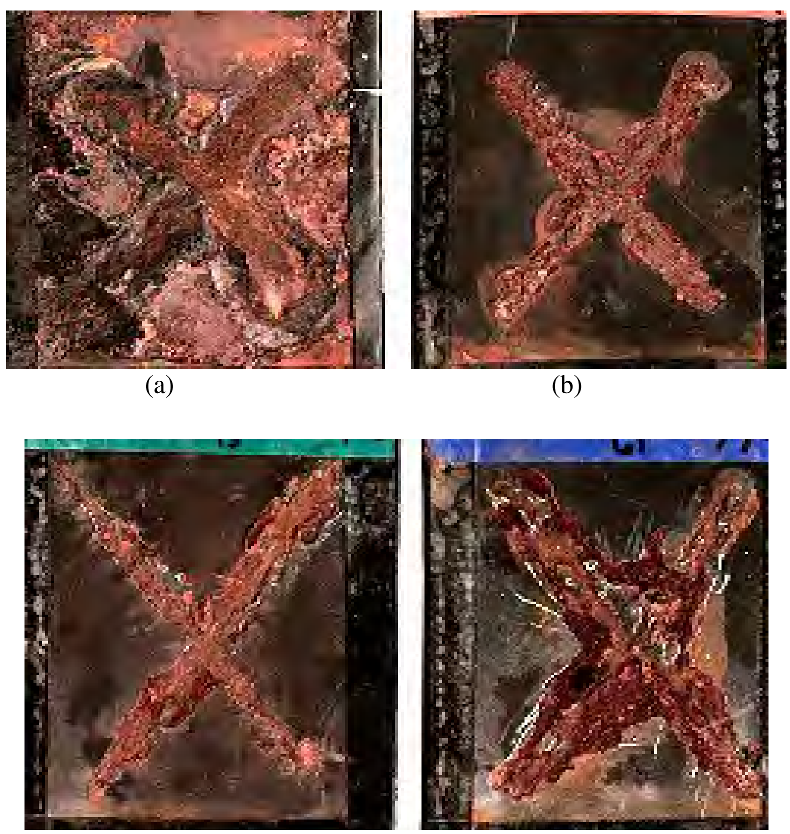
Examples of panels tested in SST and CCT are shown in Figures 1 to 4.

2.4 Summary of Section 2

Two ECOSIL water-borne primers, E-11 and AU-23, were evaluated and then further modified in this section. A solvent-borne system was also developed from scratch. The aim of this work was to develop at least one of these candidates into an effective replacement for the DoD-P-15328D wash primer. The metal substrate used here was CRS. The coatings systems used were

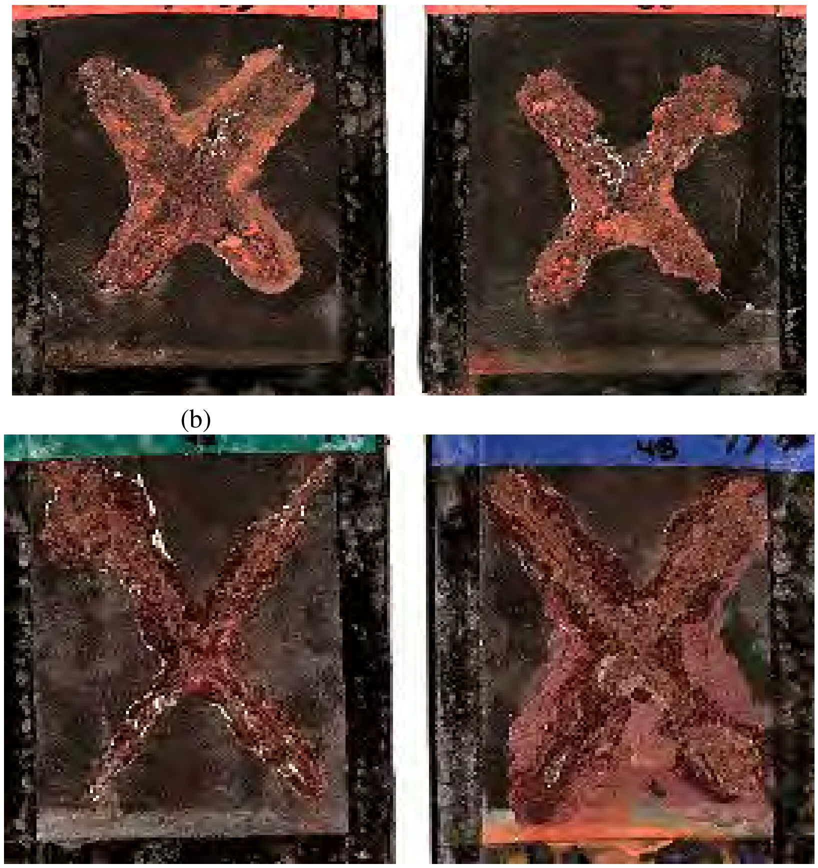
MIL-P-23377J /MIL-C-53039A and MIL-P-53022 /MIL-C-53039A. The following conclusions can be drawn.

- All tested candidates including E-11, AU-23 and its modified versions, EPZ-0 and EPZ-1, can provide excellent paint adhesion for CRS under MIL-P-23377J/MIL-C-53039A and MIL-53022/MIL-C53039A, equal to or better than DoD-P-15328D
- E-11 outperformed AU-23, EPZ-0/1 and DoD-P-15328D in the impact resistance test, but it failed in the corrosion tests.
- AU-23(A)'s performance was similar to that of DoD-P-15328D in the CCT test after 44 cycles, but underperformed DoD-P-15328D in a 500-hr SST test. EPZ-0 and EPZ-1 performed similarly to AU-23(A) in all tests.
- Although these tested candidates performed equally well to or even better than DoD-P-15328D in paint adhesion testing and in impact resistance testing, they were deemed of insufficient performance to possibly compete with DoD-P-15328D in the accelerated corrosion tests. Therefore, more developmental work was planned.



(a) (b) (c) (d)

Figure 1. CCT test (44 cycles) results for CRS panels coated with different wash primers and coated with MIL-P-53022C/MIL-C-53039A; (a) cleaned only, no wash primer, (b) DoD-P-15328D , (c) AU-23(A) and (d) E-11 (after 7 cycles).

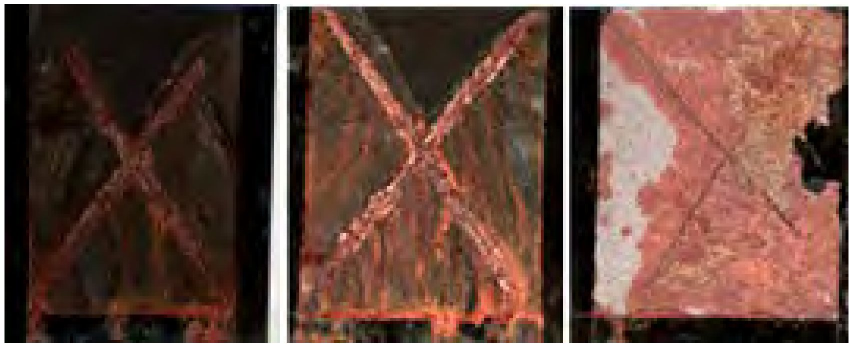


(a) (b)

(c) (d)

Figure 2. CCT test (44 cycles) results for CRS panels coated with different wash primers, topcoated with MIL-P-23377J/MIL-C-53039A; (a) cleaned only, no wash primer, (b) DoD-P-15328D, (c) AU-23(A) and, (d) E-11 (after 7 cycles).

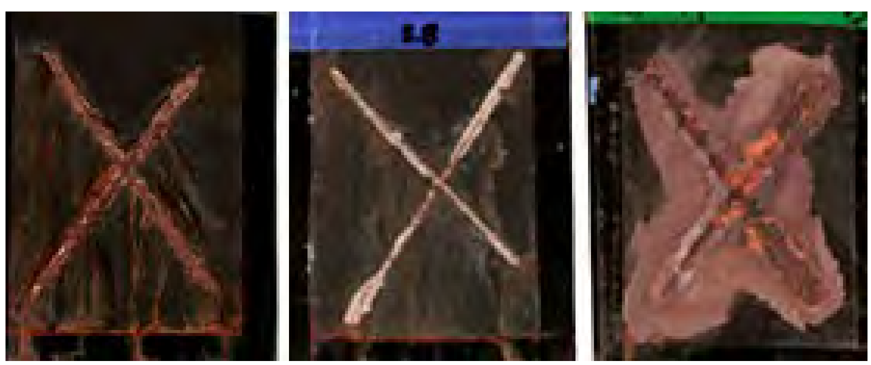
(a) 168 hrs (b) 1000 hrs (c) 500 hrs



(d) 336 hrs (e) 500 hrs (f) 168 hrs

Figure 3. SST results for CRS coated with MIL-P-53022C/MIL-C-53039A; (a) no wash primer, (b) DoD-P-15328D, (c) AU-23(A), (d) AU-23(D), (e) EPZ-0 and (f) E-11.

(a) 168 hrs (b) 1000 hrs (c) 500 hrs



(d) 336 hrs (e) 500 hrs (f) 168 hrs

Figure 4. SST results for CRS coated with with MIL-P-23377J /MIL-C-53039A; (a) no wash primer, (b) DoD-P-15328D, (c) AU-23(A), (d) AU-23(D), (e) EPZ-0 and (f) E-11.

Section 3. Evaluation and Optimization of the ECO-008 pretreatment as a Replacement of DoD-P-15328D Wash Primers

3.1 Background

In this section the work is described in which a novel pretreatment product, ECO-008, was evaluated and further optimized for use as a wash primer under military primers and topcoats. The metal substrates tested in this section were CRS and AA7075-T6. ECO-008 had earlier been developed in an NSF-funded SBIR project. In previous work, this novel pretreatment has shown a broad compatibility with many metals and paint systems.

ECO-008 is based on an advanced silane technology. The major merits of ECO-008 are summarized as follows.

(1) <u>100% VOC and HAP-free chemicals</u>. Unlike conventional silanes, which need to be hydrolyzed in advance in an aqueous media, producing alcohols (VOC) as byproducts, ECO-008 does not introduce any VOC-containing chemicals into the process. Thus, ECO-008 is greener than the conventional silane technology.

(2) <u>Improved process robustness</u>. ECO-008 delivers a flexible pretreatment process. The total number of "footprints" is from 3 to 6 stages. In industries using powder paints, for instance, a 3-stage process can be used, which includes degreasing, DI-water rinsing, and ECO-008 treatment (90 s immersion at RT). In industries using E-coating, a 6-stage process is applied. It consists of degreasing, DI-water rinsing, ECO-008 treatment (90 s immersion at RT), DI-water rinsing, DI-water rinsing. There are very few commercial pretreatment products that provide such a flexible process as offered by ECO-008. DI-water rinsing as a post rinse is mandatory for most pretreatments.

(3) <u>Compatible with multiple metals and paint systems</u>. ECO-008 offers outstanding corrosion protection performance, especially under paints. Tested paints include polyester powder paints (with TGIC and TGIC-free), cathodic e-coats and liquid epoxy paints. Metals tested include cold-rolled steel, galvanized steels and Al alloys.

(4) <u>Nano-structured film</u>. AFM characterization work confirmed that an ECO-008 film deposited on a steel surface has a thickness of 20-50 nm. A treated steel substrate shows a micro-rough surface profile, possibly indicating etching of the metal during the film forming process.

ECO-008 was evaluated under several military epoxy primers and compared with a DoD-P-15328D wash primer in several tests. In general, ECO-008 performed as well as or in some cases better than the DoD-P-15328D wash primer. The focus of current work at ECOSIL is to develop ECO-008 to a user-friendly wash primer system, especially for coating maintenance applications, in addition to marketing it as a regular pretreatment product. To date, the most successful

modified version for wash primer applications is called ECO5-1.The following reports the current status of the ECO5-1 developmental work. The evaluation of this process is still in progress and final results will be added to an updated version of this report.

3.2 Materials and Methods

Substrates: Two metal substrates were used in this section, viz., cold-rolled steel (CRS) and the aluminum alloy AA7075-T6.

ECO-008 and its modifications: An epoxy resin, Epi-Rez 5522 (from Hexion) was used as an additive in the ECO-008 solutions. It is an aqueous dispersion with 55% solids. Corrosion inhibitors were also tested as additives to ECO-008. The details of this modification work are listed in Tables 21 and 22.

Table 21. Modifications of ECO-008 with epoxy resin (in wt.%)

Sample ID	ECO-008 (1.5%)	ECO-008 (3%)	ECO-008 (6%)	Epi-rez 5522
ECO5-1	98			2
ECO5-2		98		2
ECO5-3		95		5
ECO5-4			98	2
ECO5-5			95	5

Table 22. Modifications of ECO-008 with corrosion inhibitors (in wt.%)

Sample ID	ECO-008 (1.5%)	$NaNO_2$ (15%)	Na-hexametaphosphate (1%)	Polyphosphate (1%)	Thiourea (1%)
ECO6-1	95	5			
ECO6-2	95		5		
ECO6-3	95			5	
ECO6-4	95				5

Military primers: Two military epoxy primers used in the DoD community, viz., MIL-P-53030C and MIL-P-53022D, were selected for evaluating the performance of ECO-008. Both epoxy primers are chromate-free. The former is water-borne, while the latter is solvent-borne. These military primers were manufactured by NCP Coatings Inc. and were purchased from their distributor, D&S Color Supply, Inc. The primer specifiation MIL-P-53030C is an updated version of the MIL-P-53030B specification that was used in sections 1 and 2. Likewise, MIL-P-53022D is an updated version of the MIL-P-53022C specification used in the work reported in the previous sections.

Surface treatments were as follows:

For ECO-008 only: Alkaline cleaning; city-water rinsing; DI-water rinsing; ECO-008 treatment (1.5%, spray, 60 s); DI-water rinse (massive spray, 60 s); drying (ambient, at least 30 min.); priming; curing for at least 2 weeks at room temperature.

For ECO5-1 and other modified versions: Alkaline cleaning; city-water rinsing; ECO5-1 treatment (spray, 60 s); drying (ambient, at least 30 min.); priming; curing for at least 2 weeks at room temperature.

In the above procedures the cleaning protocols were also varied. The cleaning methods included, (1) alkaline cleaning (degreasing; 2 min at 65°C), (2) acetone wiping followed by 2 min. sandpaper roughening (#150 sandpaper) and, (3) acetone wiping followed by 3 min. shot blasting (70 grit). The fully cured epoxy primer thickness was controlled at 25 to 35 µm.

Test methods: The following performance tests were conducted in this section.

1) Neutral salt spray test (SST, ASTM B117): to evaluate the corrosion resistance of the coated metal substrates in a highly corrosive environment consisting of a continuous salt fog spray with a 5% NaCl solution of pH = 6.5; the test temperature was 35°C and the humidity was 100% RH).
2) Cyclic corrosion test (CCT, GM 9540P): this is another accelerated corrosion test of coated metal substrates. The test is used in automotive industry and its result is believed to correlate better with outdoor exposure test results than those generated in the salt spray test.
3) Humidity test (ASTM D2247): this test method is used to evaluate the water resistance of organic coatings on metallic substrates. The test conditions are 38°C and 100% RH. The exposure time is 1000 hrs.
4) Adhesion test (ASTM D 3359): both dry and wet adhesion performance of the coated metal substrates were evaluated by this test which involves cross-hatching the coating followed by a tape pull. The dry paint adhesion test was done after the paints were fully cured, while the wet paint adhesion was evaluated after the painted metal substrates had been immersed in DI water for 168 hr in ambient conditions.
5) Impact resistance test (ASTM D2794): the coating flexibility and adhesion in rapid deformation was evaluated in this test. The load forces used ranged from 20 to 160 in-lb.
6) Outdoor exposure: at the Battelle site in Ponce Inlet, FL; topcoated, not scribed; in progress
7) CASS test (ASTM B368): scribed; primed only; in progress

3.3 Test results and discussion

3.3.1. Paint adhesion and impact resistance test results

ECO-008 was first tested on AA7075-T6 and CRS under the MIL-P-53030C and MIL-P-53022D primers in paint adhesion and impact resistance tests. The results are shown in Tables 23 and 24. ECO-008 performed very well, similar to the DoD-P-15328D wash primer, in both dry and wet adhesion tests and outperformed DoD-P-15328D in the impact resistance test when MIL-P-53030C was applied.

Table 23. Paint adhesion and impact resistance of ECO-008 on AA7075-T6

Sample ID	MIL-P-53030C			MIL-P-53022D		
	Dry	Wet	Impact*	Dry	Wet	Impact*
ECO-008	5B	5B	P	5B	5B	P
DoD-P-15328D	5B	5B	F	5B	5B	P

*Impact load 80 in-lb

Table 24. Paint adhesion and impact resistance of ECO-008 on CRS

Sample ID	MIL-P-53030C			MIL-P-53022D		
	Dry	Wet	Impact*	Dry	Wet	Impact*
ECO-008	5B	5B	P	5B	5B	P
DoD-P-15328D	5B	5B	F	5B	5B	P

*Impact load 80 in-lb

Tables 25 and 26 show the test results for epoxy-resin-modified ECO-008, viz., ECO5-1 to ECO5-5. All of these modified formulations performed as well as ECO-008. No performance drop was observed as a result of the modifications.

Table 27 shows the test results for corrosion-inhibitor-modified ECO-008 formulations on CRS. Apparently, these corrosion inhibitors somehow adversely affected the performance of ECO-008 in the impact resistance tests, but not in the dry/wet adhesion tests.

Table 25. Paint adhesion and impact resistance of epoxy-modified ECO-008 on AA7075-T6

Sample ID	MIL-P-53030C			MIL-P-53022D		
	Dry	Wet	Impact*	Dry	Wet	Impact*
ECO5-1	5B	5B	P	5B	5B	P
ECO5-2	5B	5B	P	5B	5B	P
ECO5-3	5B	5B	P	5B	5B	P
ECO5-4	5B	5B	P	5B	5B	P
ECO5-5	5B	5B	P	5B	5B	P
DoD-P-15328D	5B	5B	F	5B	5B	P

*Impact load 80 in-lb

Table 26. Paint adhesion and impact resistance of epoxy-modified ECO-008 on CRS

Sample ID	MIL-P-53030C			MIL-P-53022D		
	Dry	Wet	Impact*	Dry	Wet	Impact*
ECO5-1	5B	5B	P	5B	5B	P
ECO5-2	5B	5B	P	5B	5B	P
ECO5-3	5B	5B	P	5B	5B	P
ECO5-4	5B	5B	P	5B	5B	P
ECO5-5	5B	5B	P	5B	5B	P
DoD-P-15328D	5B	5B	F	5B	5B	P

*Impact load: 80 in-lb

Table 27. Paint adhesion and impact resistance of inhibitor-modified ECO-008 on CRS

Sample ID	MIL-P-53030C			MIL-P-53022D		
	Dry	Wet	Impact*	Dry	Wet	Impact*
ECO6-1	5B	5B	F	5B	5B	F
ECO6-2	5B	4B	F	5B	5B	F
ECO6-3	5B	5B	F	5B	5B	F
DoD-P-15328D	5B	5B	F	5B	5B	P

*Impact load: 80 in-lb

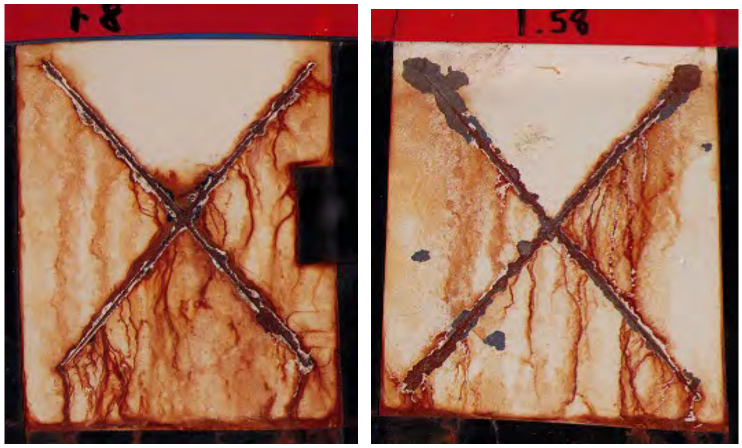
3.3.2. Accelerated corrosion test results

3.3.2.1. ECO-008 vs. DoD-P-15328D

Figure 5 shows a 1000-hr SST result for CRS panels coated with the solvent-borne MIL-P-53022D primer. Prior to priming, the panels were pretreated with ECO-008 or DoD-P-15328D. After the test, the panel with the ECO-008 pretreatment showed a little paint loss in the scribe, while the one with DoD-P-15328D exhibited a noticeable amount of paint loss. It was also noticed that the paint loss associated with DoD-P-15328D mostly occurred between the epoxy primer and the wash primer, which can be interpreted as intercoat adhesion failure, and not between the wash primer and the substrate. Figure 6 displays a 500-hr SST result for CRS panels coated with the water-borne MIL-P-53030C primer. A similar trend is observed here as in Figure 5. Again the DoD-P-15328D wash primer exhibited poor adhesion to the water-borne primer, with intercoat delamination the major cause of the failure.

The same experiments were carried out with AA7075-T6. Figures 7 and 8 show the AA7075-T6 panels after the tests. Under the water-borne primer (Figure 7) all panels performed well, with the exception of a few large blisters. ECO-008 performed on par with the DoD-P-15328D wash primer. The performance under the water-borne primer was quite different after 1440 hours of SST. The control showed many small blisters and the DoD-P-15328D wash primer had delaminated over the entire surface. ECO-008 had not delaminated or blistered, so its performance was much better than that of the DoD-P-15328D wash primer on this substrate.

It thus seems that ECO-008 is a good basis for the further optimization of a wash primer that can possibly replace the DoD-P-15328D wash primer. On CRS the performance of ECO-008 is close to that of the DoD-P-15328D wash primer, on AA7075-T6 it is much better, at least in the SST test. The DoD-P-15328D wash primer seems to have a problem with water-borne primers.

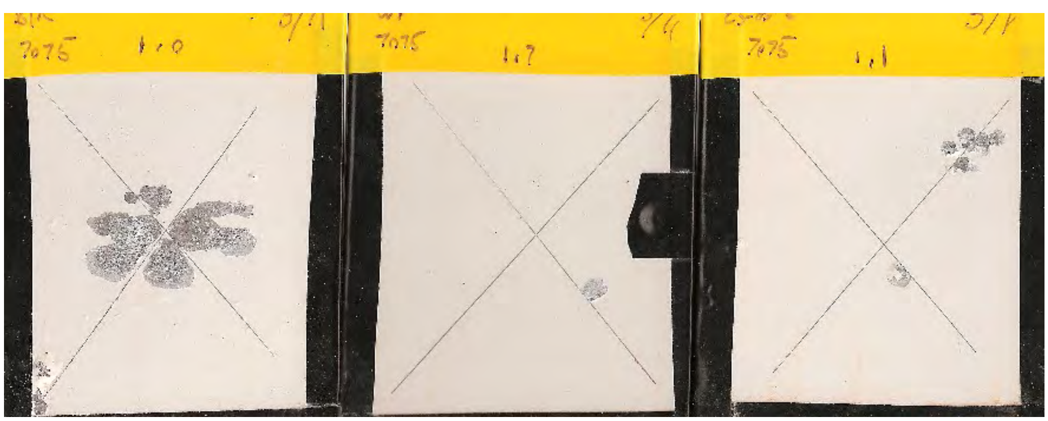


(a) (b)

Figure 5. CRS coated with MIL-P-53022D after 1000 hrs of SST; (a) ECO-008, (b) DoD-P-15328D.

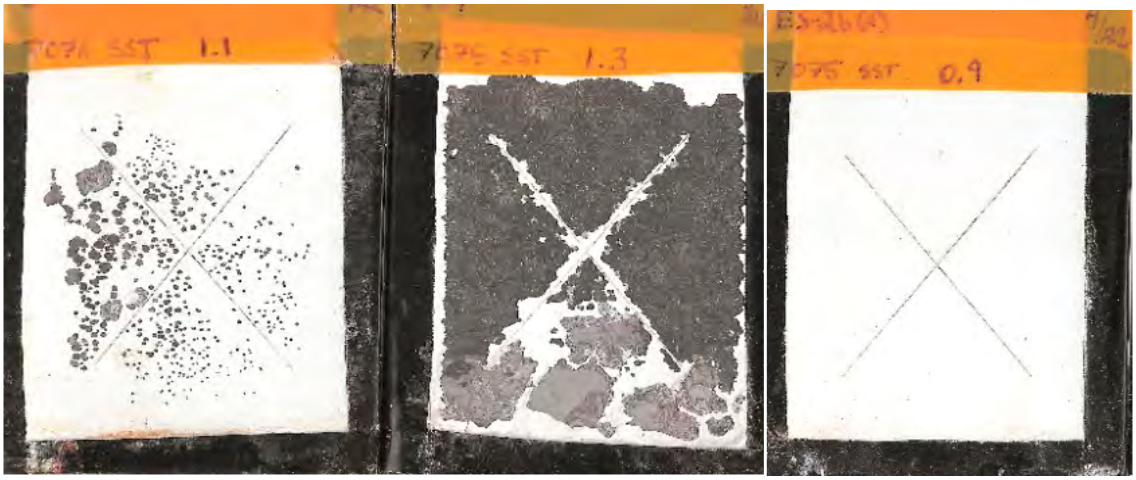
(a) (b)

Figure 6. CRS with MIL-P-53030C after 500 hrs of SST; (a) ECO-008, (b) DoD-P-15328D.



(a) (b) (c)

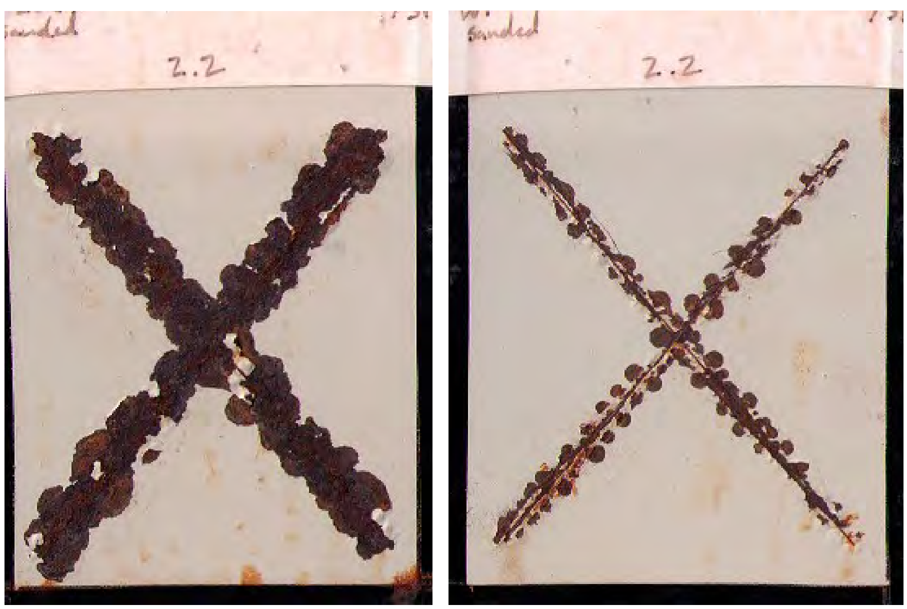
Figure 7. AA7075-T6 coated with MIL-P-53022D after 1080 hrs of SST; (a) cleaned only, no wash primer, (b) DoD-P-15328D and (c) ECO-008.



(a) (b) (c)

Figure 8. AA7075-T6 coated with MIL-P-53030C after 1440 hrs of SST; (a) cleaned only, no wash primer, (b) DoD-P-15328D and, (c) ECO-008.

ECO-008 was also tested in the CCT test. Figures 9 and 10 are 22-cycle CCT results for CRS panels primed with MIL-P-53022D and MIL-P-53030C primers, respectively. In this test, the DoD-P-15328D wash primer performed slightly better than ECO-008 under both primers. The adhesion problem with the DoD-P-15328D wash primer observed in the SST test was not observed here.



(a) (b)

Figure 9. CRS coated with MIL-P-53022D after 22 cycles of GM 9540P; (a) ECO-008, (b) DoD-P-15328D.

(a) (b)

Figure 10. CRS coated with MIL-P-53030C after 22 cycles of GM 9540P; (a) ECO-008, (b) DoD-P-15328D.

Figures 11 and 12 show the 82-cycle CCT test results for AA7075-T6 panels primed with MIL-P-53022D and MIL-P-53030C primers, respectively. With this substrate, ECO-008 performed very well under both military epoxy primers, equivalent to or better than the DoD-P-15328D wash primer. Remarkable here is the good performance of the untreated panel under the solvent-based primer (Figure 11).

(a) (b) (c)

Figure 11. AA7075-T6 coated with MIL-P-53022D after 82 cycles of GM 9540P; (a) cleaned only, no wash primer, (b) DoD-P-15328D and (c) ECO-008.

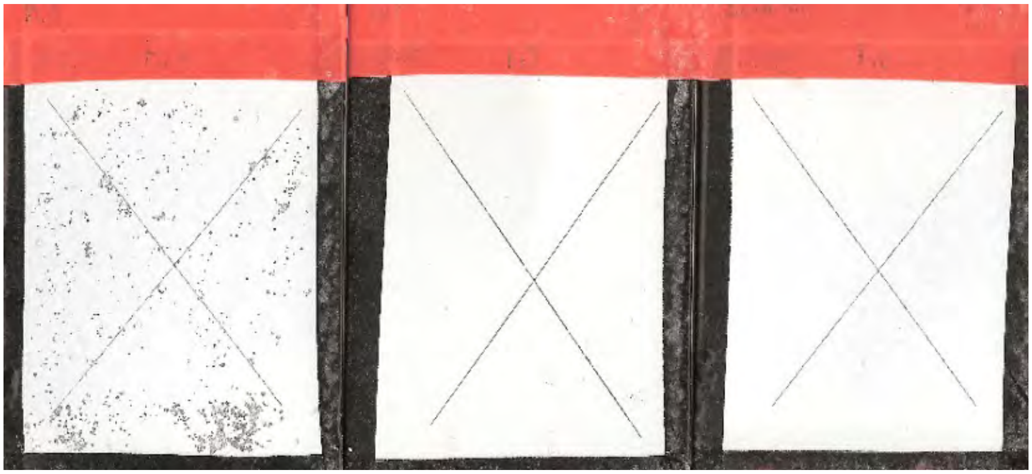

(a) (b) (c)

Figure 12. AA7075-T6 coated with MIL-P-53030C after 21 cycles of GM 9540P; (a) only, no wash primer, (b) DoD-P-15328D and (c) ECO-008.

3.3.2.2. Modified ECO-008 vs. the DoD-P-15328D wash primer

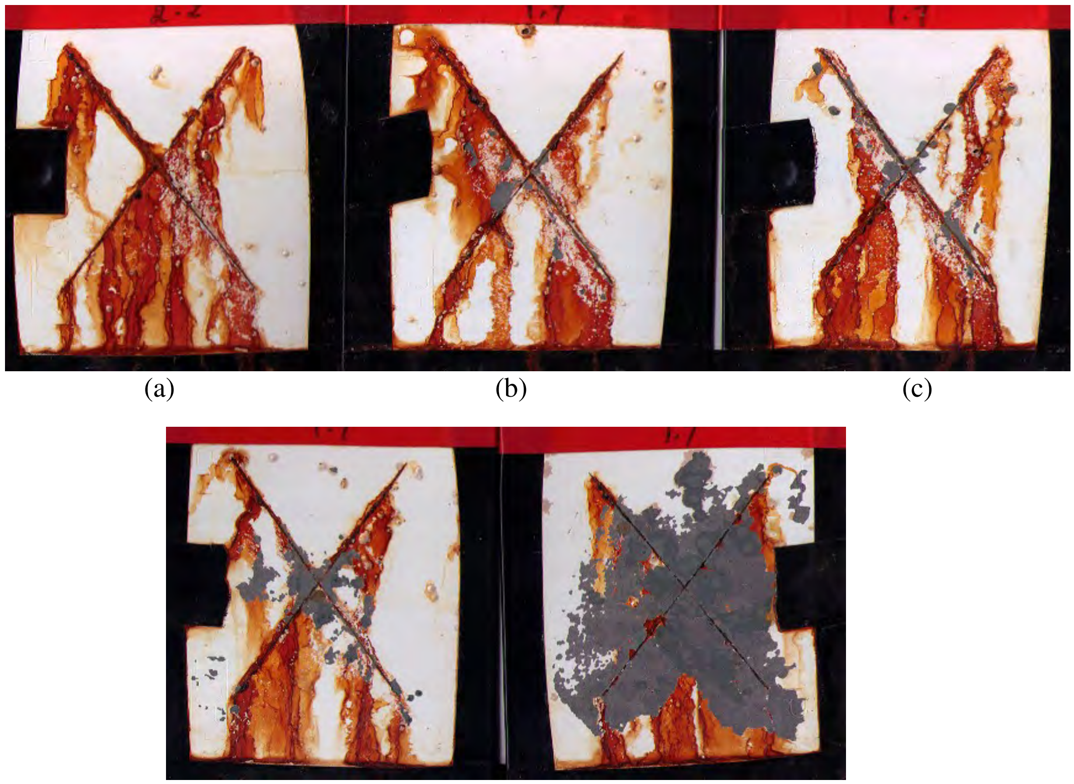
Based on the above evaluation work, it can be concluded that from a performance perspective alone, ECO-008 can be considered as an effective replacement for the DoD-P-15328D wash primer. However, the current application process of ECO-008 is complicated. For example, a few water-rinse steps, especially with DI water are involved in this process, which is undesirable in the field. To overcome this shortcoming, we initiated the following modification experiments. The modified version of ECO-008 should be more robust and user-friendly than the base ECO-008, especially in repair situations.

Figures 13 and 14 show CRS panels coated with the two military primers after two weeks of SST. The wash primers were the modified ECO-008 versions of Table 21. All wash primer candidates were spray-applied and followed by a 30-min ambient drying process *without water rinse*. In this test ECO5-1 is the best performer here. ECO5-5 performed the worst. It contained the highest amount of resin dispersed in ECO-008 at 6%, the highest concentration used here. After 500 hrs of SST, this rinse-free ECO5-1 displays the same performance as ECO-008 without resin addition.

Figure 15 shows a 168-hr SST result for ECO6-1 and ECO6-3 on CRS under MIL-P-53030C. These ECO-008 formulations were modified with corrosion inhibitors. The formulations were shown in in Table 22. All the panels showed 100% paint loss after the SST. This indicates that the corrosion inhibitors incorporated in ECO-008 adversely affected the adhesion performance of the original ECO-008 film, but not the corrosion performance. It is seen that Figure 15b actually shows less rust than the others.

The adhesion loss seen in this figure implies that wash primer should not contain any water-soluble materials, e.g., corrosion inhibitors, that can be leached out in the test conditions, such as the 100%-wet SST. Such materials will result in osmotic pressure developing under the primer ,

which lead to paint adhesion loss. It can be argued that the only corrosion inhibitor that can be tolerated in a pretreatment is chromate, because it is so effective at low concentrations. For chromate-free systems the corrosion protection relies on the barrier action and passivation properties of the pretreatment and on inhibitors in the primer, which generally do not lead to osmotic effects when they leach out.



(a) (b) (c)

(d) (e)

Figure 13. CRS coated with MIL-P-53030C after 336 hrs of SST; (a) ECO5-1, (b) ECO5-2, (c) ECO5-3, (d) ECO5-4, (e) ECO5-5; see Table 21 for formulations.

(a) (b) (c)

(d) (e)

Figure 14. CRS coated with MIL-P-53022D after 336 hrs of SST; (a) ECO5-1, (b) ECO5-2, (c) ECO5-3, (d) ECO5-4, (e) ECO5-5; see Table 21 for formulations.

(a) (b) (c)

Figure 15. CRS coated with MIL-P-53030C after 168 hrs of SST; (a) ECO6-1, (b) ECO6-2 and (c) ECO6-3; see Table 22 for formulations.

Figures 16 and 17 display tested panels after 20 cycles in the GM 9540P CCT test. All modified formulations performed well under the solvent-borne primer (MIL-P-53022D). ECO5-1 and ECO5-2 performed well under both military primers. Similar evaluation work for ECO5-1 to ECO5-5 on AA7075-T6 substrates is in progress and will be added to the updated report.

(a) (b) (c)

(d) (e)

Figure 16. CRS coated with MIL-P-53030C after 20 cycles of GM 9540P test; (a) ECO5-1, (b) ECO5-2, (c) ECO5-3, (d) ECO5-4, (e) ECO5-5; see Table 21 for formulations.

(a) (b) (c)

(d) (e)

Figure 17. CRS coated with MIL-P-53022D after 20 cycles of GM 9540P test; (a) ECO5-1, (b) ECO5-2, (c) ECO5-3, (d) ECO5-4, (e) ECO5-5; see Table 21 for formulations.

Table 28 shows the humidity test result for ECO5-1 and ECO5-5 treated CRS and AA7075-T6 under MIL-P-53030C and MIL-P-53022D. ECO5-1 performed better than ECO5-5 and was equal to DoD-P-15328D.

Table 28. 1000-hr humidity results for ECO5-1- and ECO5-5-treated CRS and AA7075-T6 under military epoxy primers (ASTM D2247)

Sample ID	MIL-P-53030C		MIL-P-53022D	
	CRS	**AA 7075-T6**	**CRS**	**AA 7075-T6**
ECO5-1	OK*	In progress	OK	In progress
ECO5-5	Blistering	In progress	OK	In progress
DoD-P-15328D	OK	In progress	OK	In progress

*No changes, no blisters

3.3.2.3. Process optimization of ECO5-1 on CRS

Based on the results shown above, ECO5-1 was selected as the best candidate to possibly replace the DoD-P-15328D wash primer. Its corrosion protection performance and its process robustness appeared to be the best among the candidates. Although ECO5-1 is derived from ECO-008, which is a pretreatment product, the application of ECO5-1 is simplified by eliminating a few process steps, such the water rinse steps commonly used in metal pretreatment applications.

Further, in coatings repair applications, alkaline cleaning is not a major cleaning method. Instead, sandpaper roughening and shot blasting followed by solvent cleaning are commonly used. Thus the performance of ECO5-1 was evaluated using variable process parameters such as cleaning methods, city-water rinsing vs. DI-water rinsing, ambient drying vs. hot-air drying, and continuous spraying vs. intermittent spraying of the wash primer candidate.

Table 29 summarizes the details of the first round of this process optimization work. Table 30 shows 96-hr SST results for CRS panels under the MIL-P-53030C primer. These CRS panels were applied with ECO5-1 using the different process variables listed in Table 29. No paint loss was observed from the scribes for all test panels, although some of them showed a few blisters in the non-scribed regions. The occurrence of this blistering seems to be associated with the drying methods only, i.e., long-time ambient drying and short-time hot-air drying. Those panels with hot-air drying did not show blistering while those prepared with ambient drying did show some blisters. Other process parameters, such as the cleaning methods, DI water as the second water rinse and wash primer application methods, did not affect the performance of ECO5-1 significantly, illustrating a very robust process.

The details of the 2nd round of process optimization work done with CRS under the MIL-P-53022D primer are presented in Table 31. Here, two cleaning methods were compared on, viz., solvent cleaning and mechanical cleaning (sandpaper roughening and shot blasting). The DI-water rinse step was also eliminated before the ECO5-1 application. The CRS panels were exposed to the SST test for 240 hrs and are shown in Figure 18. Two process parameters are

compared: (1) the drying method, RT (room temperature) drying vs. HA (hot air) drying; (2) the surface preparation method, shot blasting vs. sandpaper roughening.

Table 29. Optimization of process parameters for ECO5-1 on CRS under MIL-P-53030C

Process ID	Cleaning	Rinse 1	Rinse 2	Wash Primer Application	Drying
P-1	alkaline	CW[1]	DIW[2]	immersion/120"	RT[3]
P-2	alkaline	CW	-	immersion/120"	RT
P-3	alkaline	CW	DIW	Spray/120" (C)[5]	RT
P-4	alkaline	CW	-	Spray/120" (C)	RT
P-5	alkaline	CW	DIW	Spray/120" (C)	HA[4]
P-6	alkaline	CW	-	Spray/120" (C)	HA
P-7	alkaline	CW	DIW	Spray/120" (10"S/20" for 4 times)[6]	RT
P-8	alkaline	CW	-	Spray/120" (10"S/20" for 4 times)	RT
P-9	alkaline	CW	DIW	Spray/120" (10"S/20" for 4 times)	HA
P-10	alkaline	CW	-	Spray/120" (10"S/20" for 4 times)	HA
P-11	Acetone	-	-	Spray/120" (10"S/20" for 4 times)	RT
P-12	Acetone/rough[7]	CW	-	Spray/120" (10"S/20" for 4 times)	RT
P-13	Acetone/shot[8]	CW	-	Spray/120" (10"S/20" for 4 times)	RT

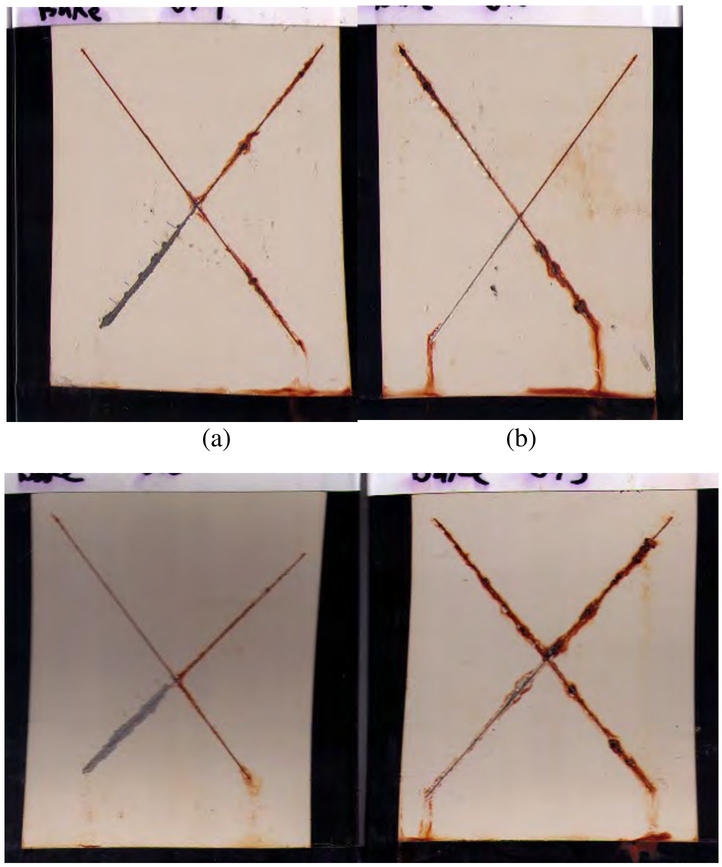
1. CW: City Water rinse
2. DIW: Deionized Water rinse
3. RT: Room-Temperature drying
4. HA: Hot Air drying
5. Spray/120"(C): Continuous spraying for 120 s
6. Spray/120" (10"S/20" for 4 times): Continuous spraying for 10 s; stop for 20 s; repeat 3 times
7. Acetone/rough: Acetone cleaning, followed by sandpaper roughening using sandpaper #150
8. Acetone/shot: Acetone cleaning, following by steel shot blasting

Table 30. 96-hr SST results for ECO5-1 on CRS under MIL-P-53030C
(ECO5-1 was applied using the processes shown in Table 29)

Process ID	ECO5-1-treated CRS surface	96-hr SST
P-1	Slightly brownish	No paint loss, no blisters
P-2	Slightly brownish	No paint loss, no blisters
P-3	Slightly brownish	No paint loss, a few blisters
P-4	Slightly brownish	No paint loss, a few blisters
P-5	Original appearance	No paint loss, no blisters
P-6	Original appearance	No paint loss, no blisters
P-7	Slightly brownish	No paint loss, a few blisters
P-8	Slightly brownish	No paint loss, a few blisters
P-9	Original appearance	No paint loss, no blisters
P-10	Original appearance	No paint loss, no blisters
P-11	Slightly brownish	No paint loss, a few blisters
P-12	Slightly brownish	No paint loss, a few blisters
P-13	Slightly brownish	No paint loss, a few blisters

Table 31. Process optimization for ECO5-1-treated CRS under MIL-P-53022D

Process ID	Cleaning	rinse	treatment	drying
P-12	Acetone/rough	CW	Spray/120" (10"S/20" for 4 times)	RT
P-13	Acetone/shot	CW	Spray/120" (10"S/20" for 4 times)	RT
P-12a	Acetone/rough	CW	Spray/120" (10"S/20" for 4 times)	HA
P-13a	Acetone/shot	CW	Spray/120" (10"S/20" for 4 times)	HA



(a) (b)

(c) (d)

Figure 18. CRS coated with ECO5-1 and MIL-P-53022D after 240 hrs of SST test; (a) P12, (b) P12a, (c) P13 and (d) P13a of Table 31.

In Figure 18, P12a and P13a were both hot-air-dried aired after the ECO5-1 treatment, while P12 and P13 were RT dried (Table 31). The P12a and P13a surfaces after hot-air drying retained their original shiny appearance whereas that of P12 and P13 was slightly brownish after RT drying. It is also observed in Figure 18 that both P12a and P13a display no paint loss from the scribe while P12 and P13 have a small amount of paint loss. This indicates that hot-air drying seems to enhance the performance of ECO5-1. It also minimizes flash rust formation. It can further be concluded that the surface preparation method, viz., sandpaper roughening vs. shot blasting, does

not have a significant effect on the performance of ECO5-1. Similar work with AA7075-T6 is in progress and will be included in the updated report.

Table 32 shows the performance test results for ECO5-1-pretreated CRS panels subsequently coated with MIL-P-53030C or MIL-P-53022D in the SST and CCT tests. The surface preparation methods compared here were, (1) acetone degreasing, sandpaper roughening with #150 sandpaper, followed by city water rinsing, (2) alkaline degreasing, followed by city water rinsing and, (3) acetone degreasing, shot blasting, followed by city-water rinsing. Figure 19 shows the panels coated with the WB primer MIL-P-53030C after the SST test.

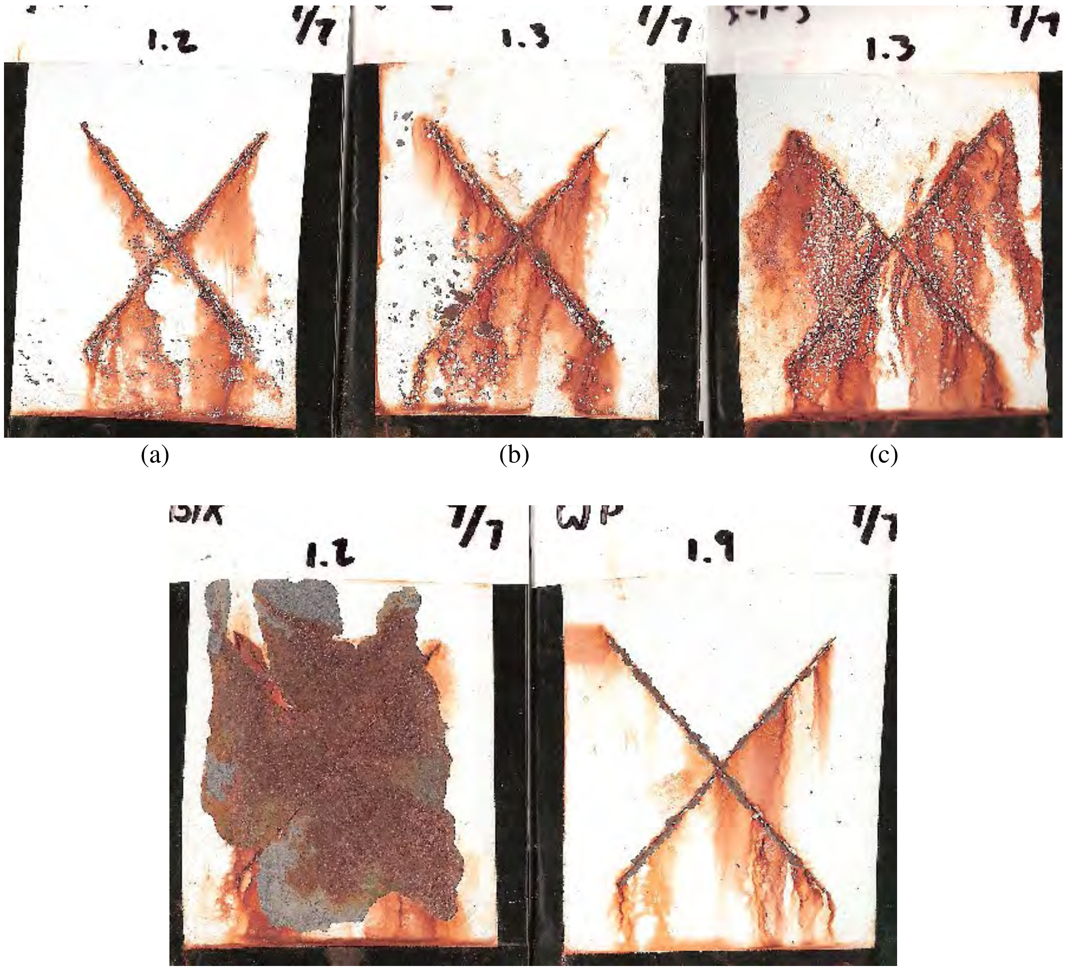
Table 32. Test results for ECO5-1-treated CRS under two military primers with the surface preparation method varied (creepage in mm)

Sample ID	Surface preparation	MIL-P-53030C		MIL-P-53022D	
		SST (336 hrs)	CCT (20 cycles)	SST (500 hrs)	CCT (20 cycles)
51-1	Sandpaper roughening	See Figure 19	2	0	1
51-2	Alkaline degreasing		1.75	0	1.75
51-3	Shot blasting		2	0	1.75
Untreated CRS	Shot blasting		3	2.5	8.5
DoD-P-15328D	Shot blasting		1	0	0.75

The results of Table 32 and Figure 19 indicate a very good performance of the proposed wash primer replacement. In all cases the untreated CRS panels are considerably worse, as can be expected. In the SST test ECO5-1 displays a slight effect of the cleaning process under the WB primer, with sand paper roughening showing the least delamination and a performance closest to that of the DoD-P-15328D wash primer (Figure 19). In the CCT test under the WB primer and in both tests under the SB primer, the performance of ECO5-1 is very close to that of the DoD-P-15328D wash primer, which is remarkable for such a thin film which contains no etchant such as phosphoric acid, and no corrosion inhibitor such as chromate.

It can also be concluded that the conversion from the original ECO-008 pretreatment to the ECO5-1 wash primer has resulted in a process that is robust and almost independent of the metal pretreatment and the application conditions. This process, therefore, is amenable to actual field use. The results presented indicate that optimum results are obtained if the metal is sandpaper roughened and the wash primer is applied by continuous spraying and then dried quickly using hot air. Rinsing is not necessary. This application process improves performance and minimizes flash rust formation. The new wash primer performs well under chromate-free WB and SB primers, but the SST and CCT performance is better under SB primers. This conclusions is also valid for the DoD-P-15328D wash primer, which has adhesion issues with WB primers.

Tests as shown in Table 32 for the aluminum alloy AA7075-T6 are in progress and will be included in the updated version of the report.



(a) (b) (c)

(d) (e)

Figure 19. 336-hr SST results for ECO5-1-treated CRS panels under the WB primer MIL-P-53030C; the surface preparation method was varied, see Table 32; (a) 51-1, (b) 51-2, (c) 51-3, (d) untreated, (e) shot-blasted and coated with DoD-P-15328D (Table 32).

3.4. Summary of Section 3

In this part of the work, a novel pretreatment recently developed at ECOSIL, ECO-008, was tested under the MIL-P-53022D and MIL-P-53030C primers. In general, ECO-008 performed equally well and in some cases better than the DoD-P-15328D wash primer. Further modification work was then conducted on ECO-008, with the aim of developing it into a user-friendly version that can be used in the field as a wash primer. The modifications included addition of water-dispersed resins to ECO-008, eliminating the DI-water rinse steps before and after the pretreatment, testing intermittent spraying method, varying the drying method and testing several cleaning methods prior to wash primer deposition. Based on the outcome of these modifications the following conclusions can be drawn.

- ECO5-1 is based on the ECO-008 pretreatment, but is more user-friendly in the field, as it can be applied in a shorter and simpler process than ECO-008 with minimal surface preparation and no rinsing requirements.
- The performance of ECO5-1 is comparable to that of the DoD-P-15328D wash primer in SST and CCT tests for use on CRS, but exceeds the performance of the DoD-P-15328D wash primer on AA7075-T6.
- ECO-5-1 outperforms the DoD-P-15328D wash primer in adhesion and impact resistance tested on both metals that were used.
- The following work plan is scheduled for ECO5-1:
  1. To conduct Florida outdoor exposure tests for CRS under MIL-P-53022D and MIL-P-53030C and with two CARC topcoats, MIIL-DTL-53039C and MIL-DTL-64159A; this is is progress and will be completed by the end of 2012; section 4 presents the 6-months data.
  2. To conduct the CASS test (ASTM B368) for AA7075-T6 under MIL-P-53022D and MIL-P-53030C; this is also in progress and will be completed by the end of August 2011.
  3. Complete several tests with AA7075-T6 in the CCT; such tests require 80 or more cycles of one day each for this alloy; they are expected to be completed in the Fall of 2011 and will be included in the updated version of this report.

Section 4. Outdoor Exposure of Painted Panels

4.1 Background

Promising candidate wash primers were shipped in triplicate to the Battelle Florida Materials Research Facility in Ponce Inlet, FL, which is just south of Daytona Beach. The climate there is subtropical. The test is scheduled for a 2-year exposure term. The candidate wash primers included AU-23(C), EPZ-0 and ECO-008, all on CRS. The controls were the DoD-P-15328D wash primer and zinc-phosphated CRS (C710, spray zinc phosphate from PPG Industries). The dimensions of the panels were 10x15 cm. A second batch of panels was shipped in July 2011. These panels included the ECO5-1 wash primer applied with various cleaning procedures.

4.2 Test Results

Table 33 lists the coating systems on CRS that are currently being exposed. They were not scribed and the backside and edges of the panels were coated with a UV-resistant tape. Two CARC PU topcoats were used, viz., 1-K, SB MIL-DTL-53039C and 2-K, WB MIL-DTL-64159A. The status of the panels is updated every 3 months for up to 2 years. After the first 6 months, most systems looked intact. No corrosion or blistering has been identified at this point, except for some pitting here and there. Figure 20 shows the panels on the racks and Figures 21 to 40 show photographs of the individual test panels after 6 months of exposure.

Table 33. Florida outdoor exposure test schedule

Pretreatment	Coating system	3-m	6-m	9-m	12-m	15-m	18-m	21-m	24-m
DoD-P-15328D (Control 1)	53030C/53039C	OK	OK						
	53030C/64159A	OK	OK						
	53022D/53039C	OK	OK						
	53022D/64159A	OK	OK						
C710 (Control 2)	53030C/53039C	OK	OK						
	53030C/64159A	OK	OK						
	53022D/53039C	OK	OK						
	53022D/64159A	OK	OK						
AU-23(D)	53030C/53039C	OK	OK						
	53030C/64159A	OK	OK						
	53022D/53039C	OK	OK						
	53022D/64159A	OK	OK						
EPZ-0	53030C/53039C	OK	Pits						
	53030C/64159A	OK	OK						
	53022D/53039C	OK	OK						
	53022D/64159A	OK	OK						
ECO-008	53030C/53039C	OK	OK						
	53030C/64159A	OK	OK						
	53022D/53039C	OK	OK						
	53022D/64159A	OK	OK						

– completed – to be completed OK: No corrosion activities

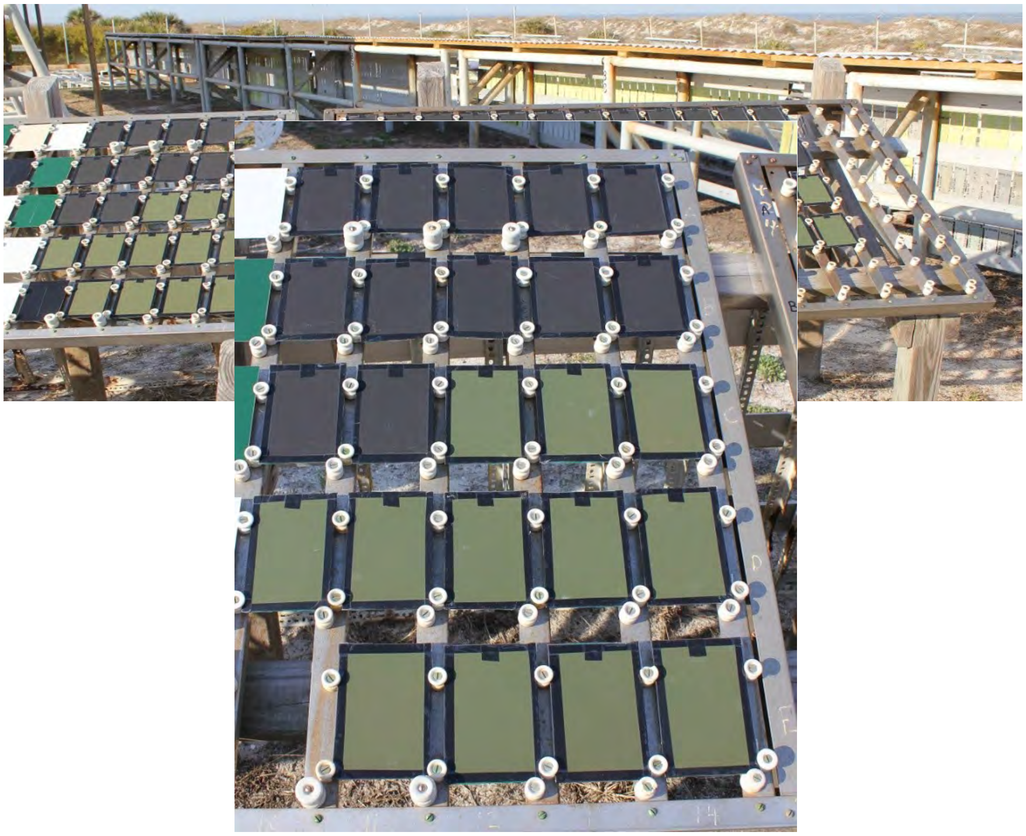


Figure 20. Exposure site at Battelle Florida Materials Research Facility, Ponce Inlet, FL

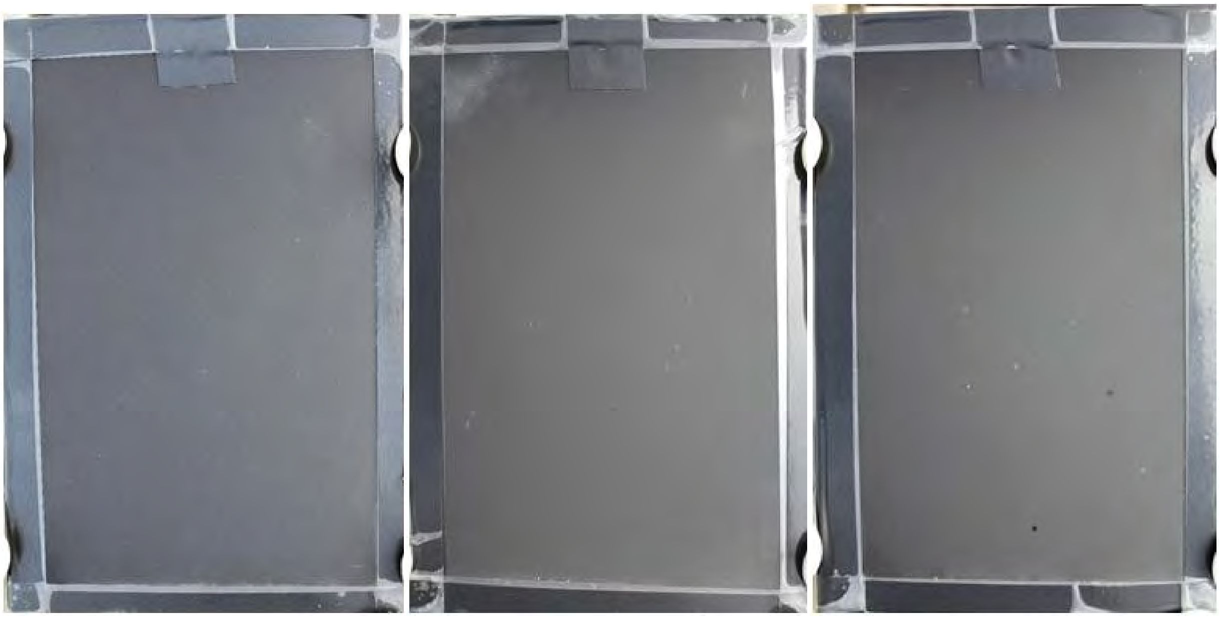


Figure 21. CRS panels coated with DOD-P-15328D/MIL-DTL-53030C/MIL-DTL-53039C after 6 months

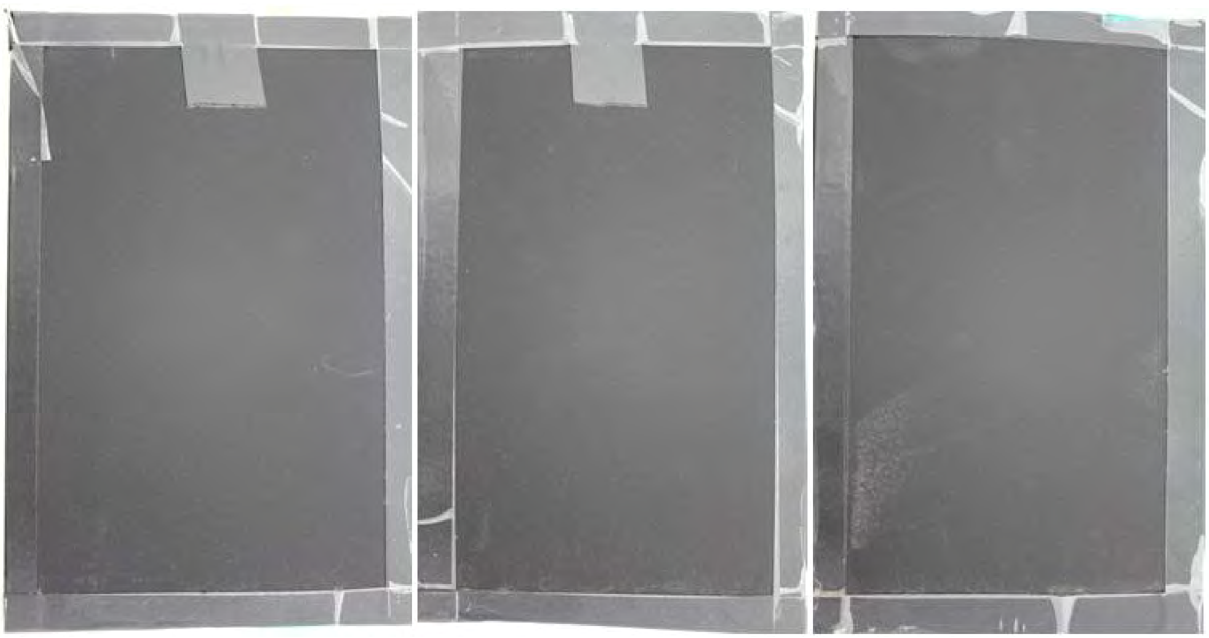


Figure 22. CRS panels coated with C710/MIL-DTL-53030C/MIL-DTL-53039C after 6 months

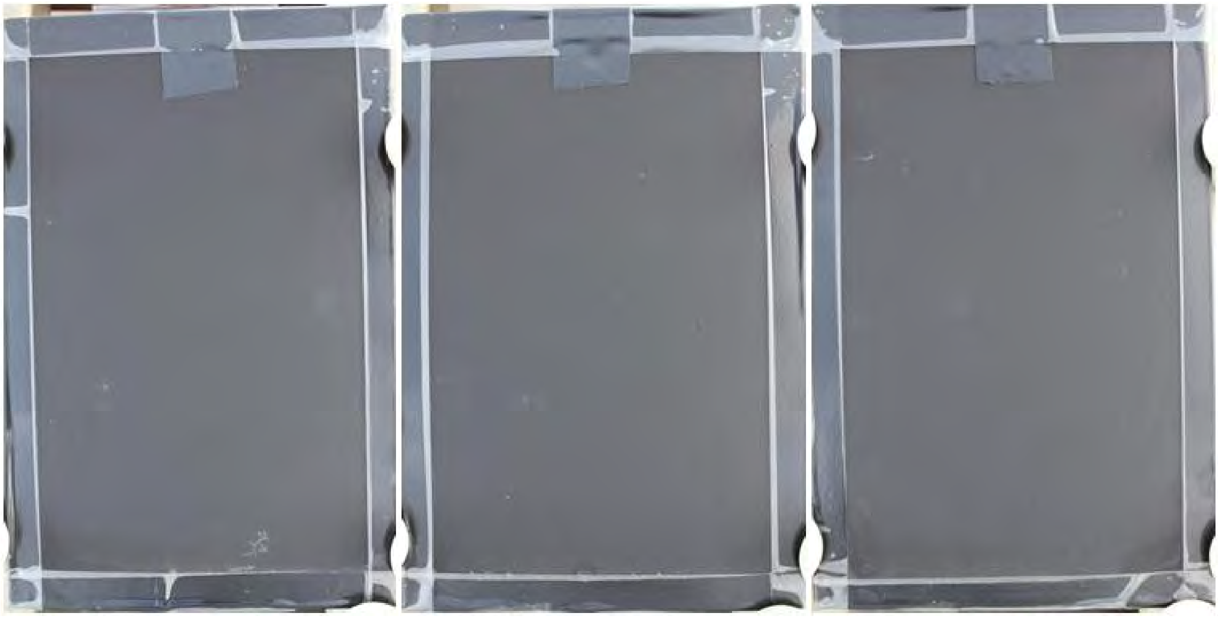


Figure 23. CRS panels coated with AU-23(C)/MIL-DTL-53030C/MIL-DTL-53039C after 6 months

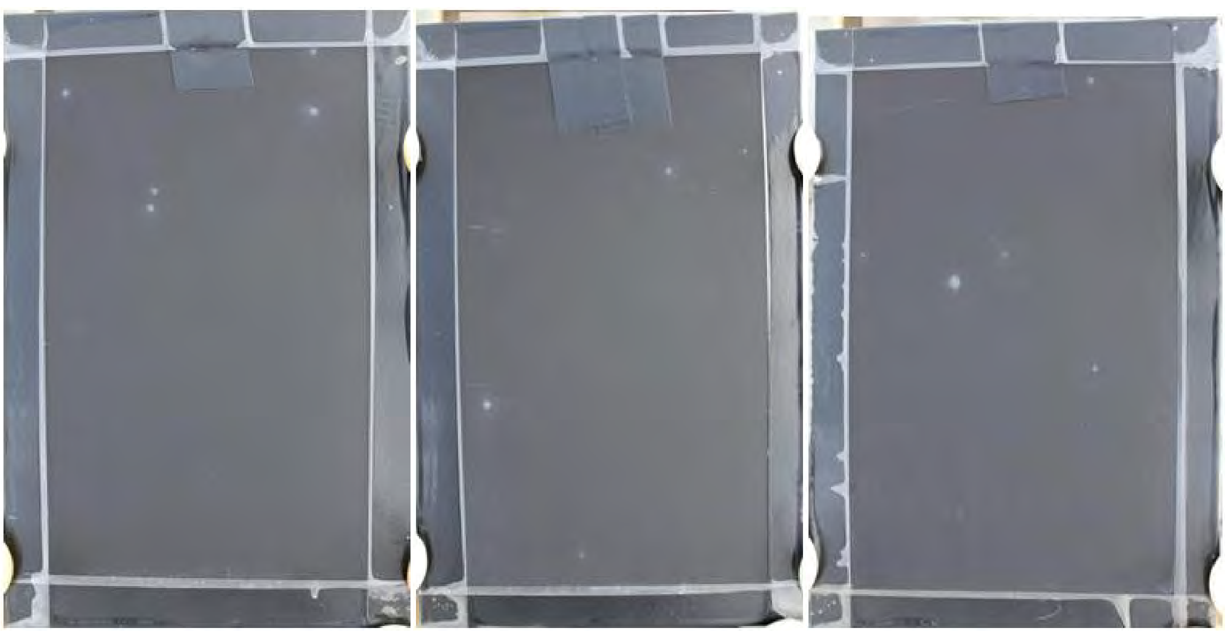


Figure 24. CRS panels coated with EPZ-0/MIL-DTL-53030C/MIL-DTL-53039C after 6 months

Figure 25. CRS panels coated with ECO-008/MIL-DTL-53030C/MIL-DTL-53039C after 6 months

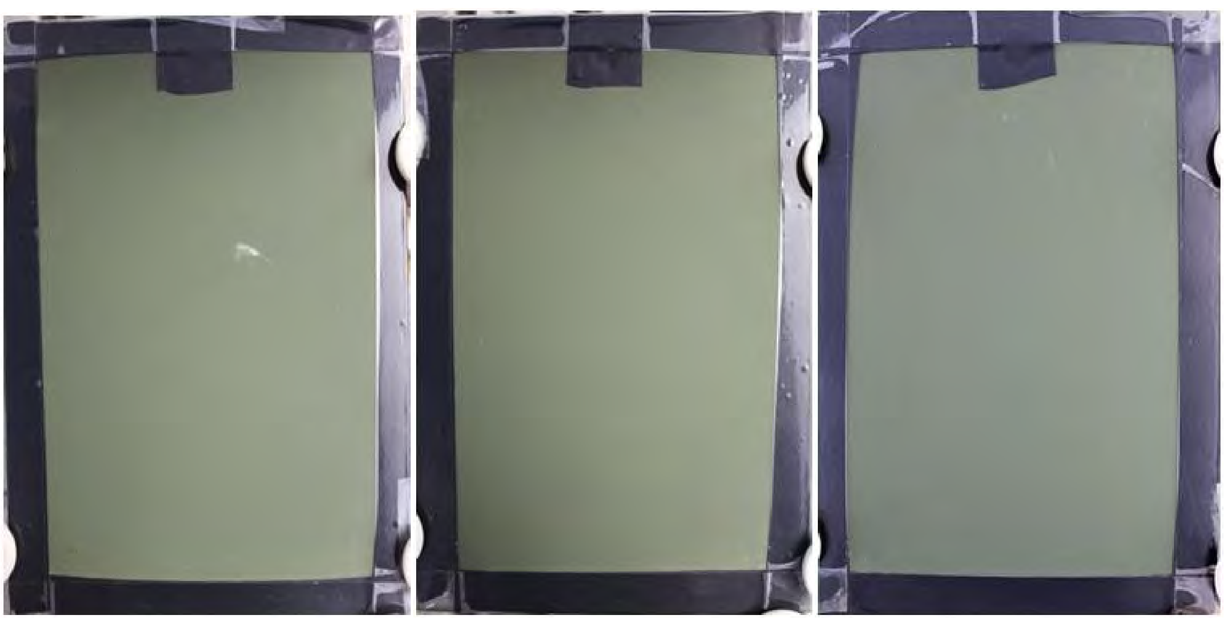


Figure 26. CRS panels coated with DOD-P-15328D/MIL-DTL-53030C/MIL-DTL-64159A after 6 months

Figure 27. CRS panels coated with C710/MIL-DTL-53030C/MIL-DTL-64159A after 6 months

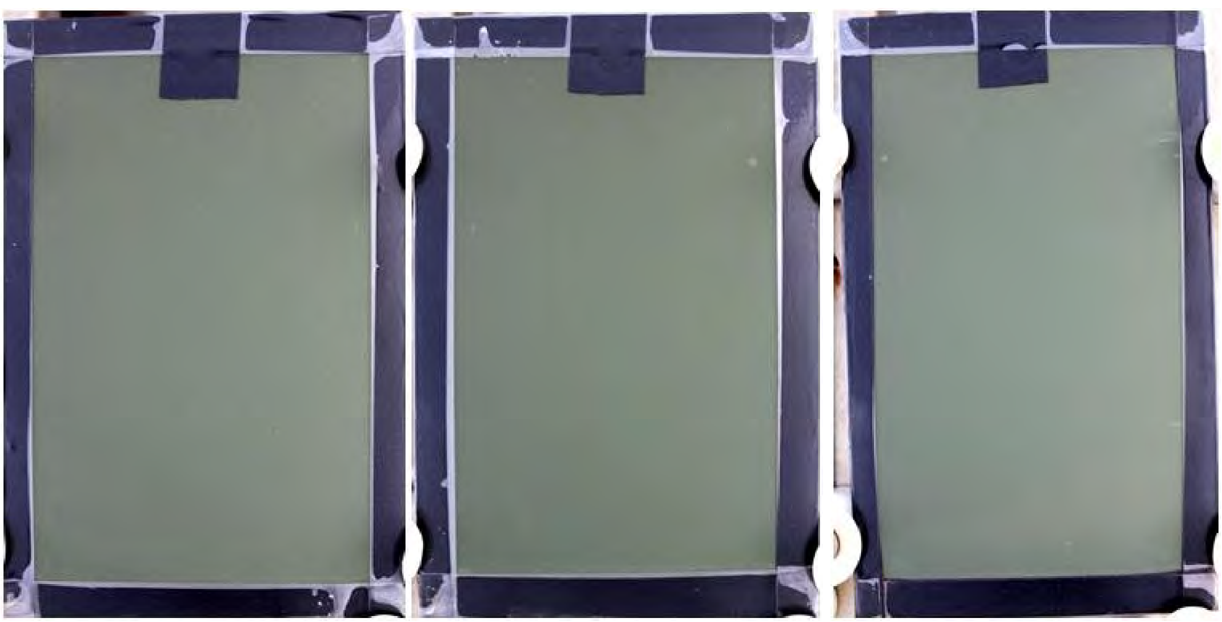


Figure 28. CRS panels coated with AU-23(D)/MIL-DTL-53030C/MIL-DTL-64159A after 6 months

Figure 29. CRS panels coated with EPZ-0/MIL-DTL-53030C/MIL-DTL-64159A after 6 months

Figure 30. CRS panels coated with ECO-008/MIL-DTL-53030C/MIL-DTL-64159A after 6 months

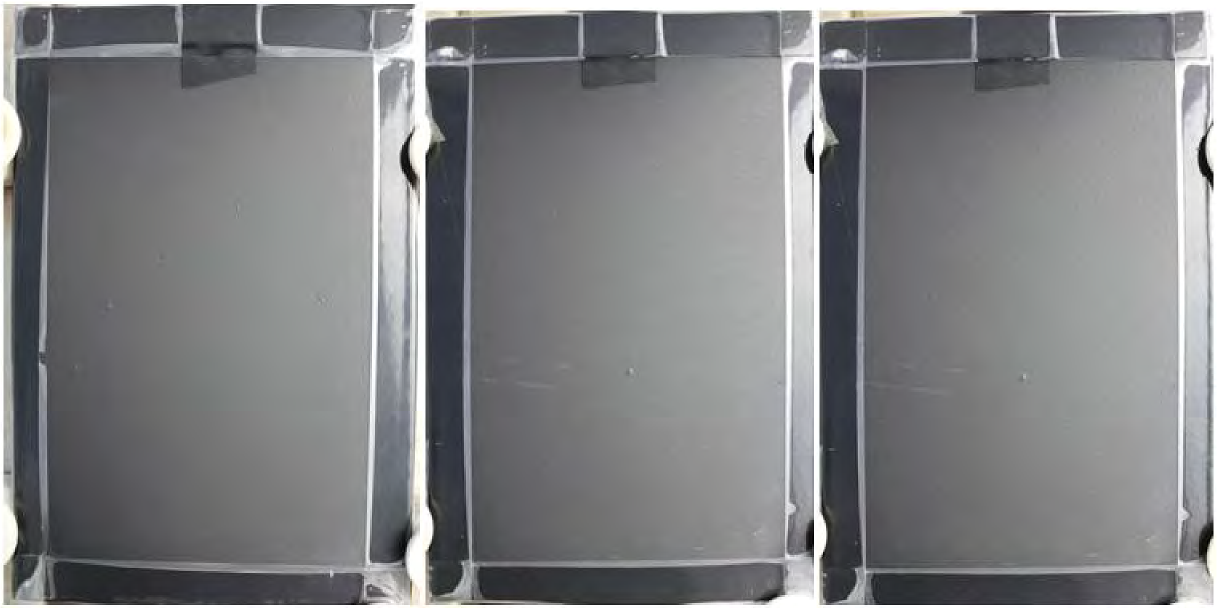


Figure 31. CRS panels coated with DoD-15328D/MIL-DTL-53022D/MIL-DTL-53039C after 6 months

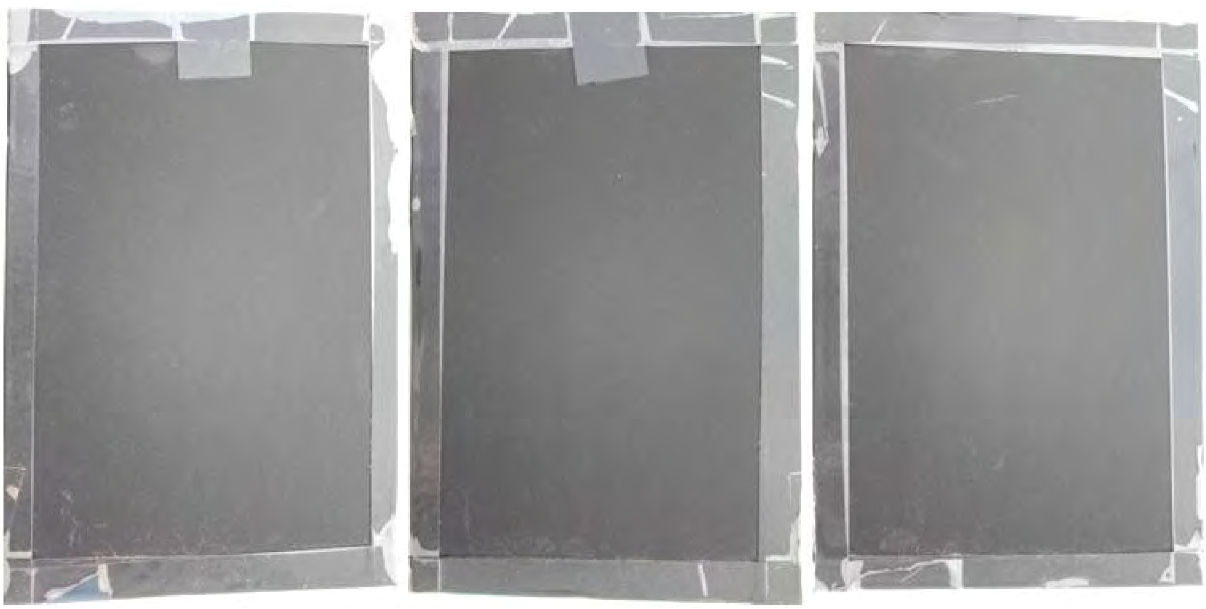


Figure 32. CRS panels coated with C710/MIL-DTL-53022D/MIL-DTL-53039C after 6 months

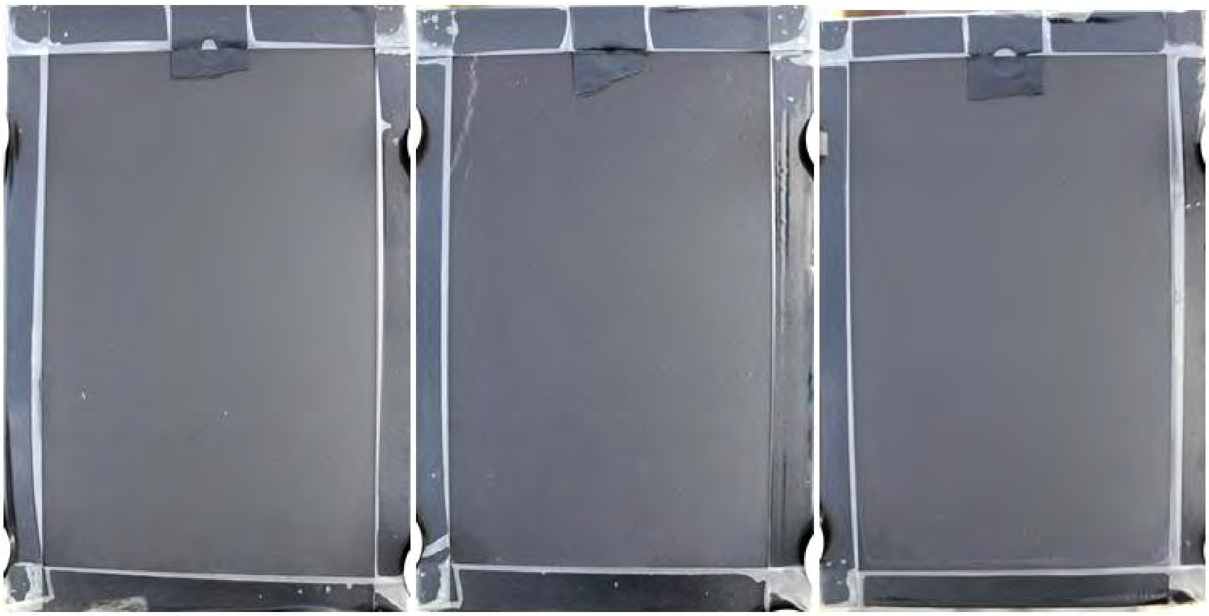


Figure 33. CRS panels coated with AU-23(C)/MIL-DTL-53022D/MIL-DTL-53039C after 6 months

Figure 34. CRS panels coated with EPZ-0/MIL-DTL-53022D/ MIL-DTL-53039C after 6 months

Figure 35. CRS panels coated with ECO-008/MIL-DTL-53022D/ MIL-DTL-53039C after 6 months

Figure 36. CRS panels coated with DoD-15328D/MIL-DTL-53022D/ MIL-DTL-64159A after 6 months

Figure 37. CRS panels coated with C710/MIL-DTL-53022D/MIL-DTL-64159A after 6 months

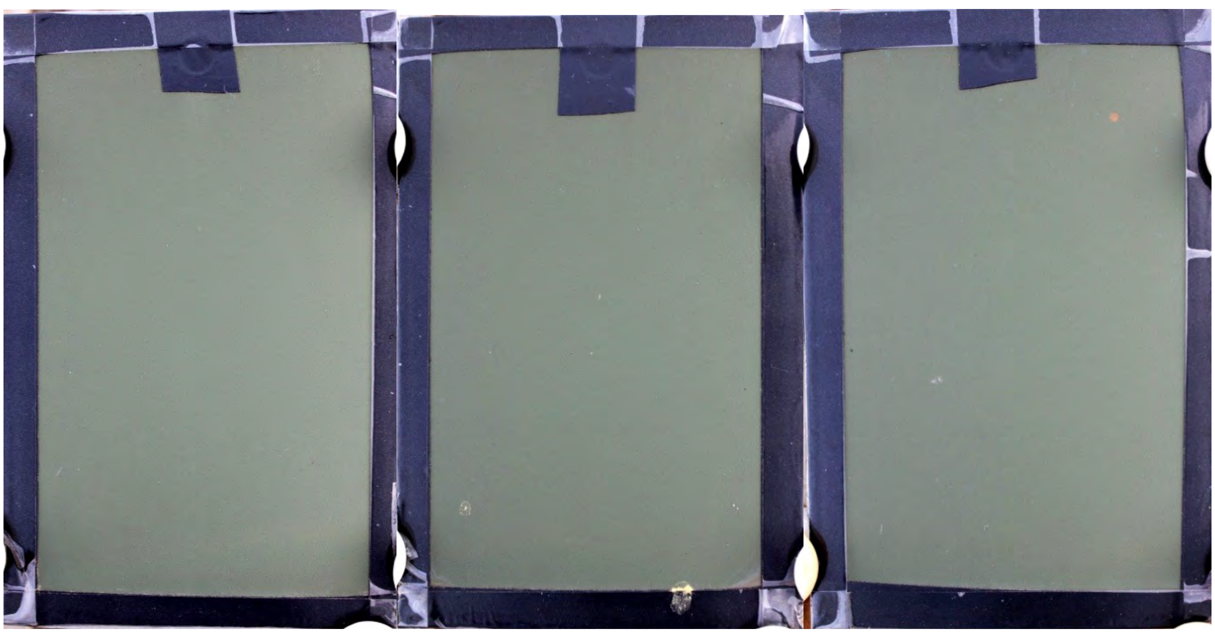


Figure 38. CRS panels coated with AU-23(D)/MIL-DTL-53022D/MIL-DTL-64159A after 6 months

Figure 39. CRS panels coated with EPZ-0/MIL-DTL-53022D/MIL-DTL-64159A after 6 months

Figure 40. CRS panels coated with ECO-008/MIL-DTL-53022D/MIL-DTL-64159A after 6 months

5. Section 5. Characterization of Coated Metal Systems

5.1 Test Methods

The candidate wash primers in this project were characterized in this part of the work using various characterization tools. The results are reported in this section.

1) EDX: CRS samples treated with ECO-008 and ECO5-1 were examined by EDX at the University of Cincinnati. The working voltage was 20 kV. The instrument was a Philips XL30 ESEM used at an accelerating voltage of 20 kV.

2) Coating weight measurement: the coating weights of ECO5-1 and ECO-008 were measured on AA6061-T6 in accordance with the method described in MIL-DTL-81706A.

3) VOC measurement: the VOC content of ECO-008, ECO5-1, AU-23 and EPZ-0 were measured according to EPA method 24A. The samples were evaluated by Calvary Industries, Inc.

4) Electrochemical Impedance Spectroscopy (EIS): The electrochemical performance of candidate wash primers were measured on a weekly basis using a 0.5% NaCl solution (pH = 6.5) as a function of exposure time in the GM9540P test. They were not scribed and not topcoated.

5) Fourier-Transform Infrared Spectroscopy (FTIR): Films of the DoD-P-15328D wash primer, ECO-008 and ECO5-1 were characterized by FTIR using a Spectrum 100 instrument from Perkin Elmer.

5.2 Results and Discussion

5.2.1. EDX analysis

The EDX data of the two types of films are shown in Table 34. Since Fe is from the substrate and probably not incorporated in the film, two columns are also given in which the analysis is recalculated with the exclusion of the Fe signal.

Table 34. EDX results for ECO-008 and ECO5-1 films on CRS

Element	ECO-008 (wt.-%)	ECO-008 (no Fe)	ECO5-1 (wt.-%)	ECO5-1 (no Fe)
C	4.7	24.0	35.9	74.0
N	1.1	5.6	1.0	2.1
O	2.4	12.4	3.7	7.6
F	5.1	26.0	3.4	6.9
Si	0.1	0.5	0.3	0.6
Zr	6.2	31.5	4.2	8.6
Fe	80.4	-	51.6	-

The results indicate that ECO5-1 contains much more organics, as expected. As a result, all

other elements are detected at lower amounts, including Fe from the substrate, since the ECO5-1 film is thicker than the ECO-008 film. The elements Zr, F, Si and N are known components of ECO-008.

5.2.2. Coating Weight measurements

The coating weight measurements were conducted by the standard procedure described in MIL-DTL-81706A. Two replicates of ECO-008 and ECO5-1 were prepared on aluminum alloy 6061-T6 of 7.5x10 cm dimensions. The panels were were dried for 1 to 1.5 hours at room temperature and then weighed. Next they were immersed in 35% nitric acid solution for 1 minute while using a clean cotton swab to remove the coating. After removal of the coatings, the coupons were rinsed thoroughly in de-ionized water, hot-air dried and reweighed. The weight of the chemical conversion film in milligrams per square foot or m^2 is then calculated as follows:

Film Weight = (W1 - W2) x 6 for milligrams/ft^2 (64.5 for milligrams per m^2)
Where: W1 = Initial weight in milligrams, and W2 = Final weight in milligrams

Table 35. Coating Weight measurements for ECO-008 and ECO5-1 on AA6061

Sample ID	Coating Weight (mg/ft^2)	Coating Weight (mg/m^2)
ECO-008 Rinsed	3.4	36.6
ECO-008 Not Rinsed	4.2	45.2
ECO5-1 Rinsed	5.3	44.1
ECO5-1 Not Rinsed	8.0	92.6

These results, shown in Table 35 indicate very low coating weights, less than conventional wash primers. The non-rinsed versions have slightly higher coating weight, especially the ECO5-1 system, which contains the organic resin additive.

5.2.3. VOC measurements

Table 36 shows the VOC values for different wash primers/pretreatments. ECO-008 has zero VOC, while ECO5-1 with a small amount of epoxy resin as an additive contains a VOC of 3 g/liter. The VOC content in AU-23 is also significantly lower than the current wash primer, DoD-P-15328D, which has 777 g/L VOC. This is mainly the solvent isopropanol.

Table 36. VOC values of various systems

Sample ID	VOC (lb/gallon)	VOC (g/L)
ECO-008	0	0
ECO5-1	0	3
AU-23	0.3	36
DoD-P-15328D	6.5	777

5.2.4. EIS measurements

Initially the EIS measurements were carried out as is commonly done by electrochemical

researchers, namely by exposing fully coated systems to a solution of aerated 5% NaCl. The modulus of the impedance of the total system or some other electrochemical parameter is then followed over time and measured at regular intervals, for instance daily or weekly. The results are shown in Figure 41a-d.

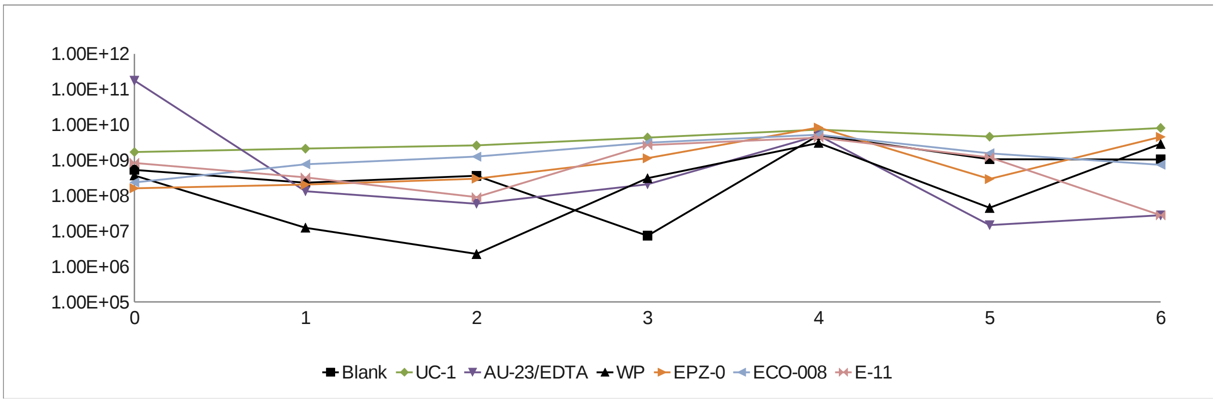


Figure 41a

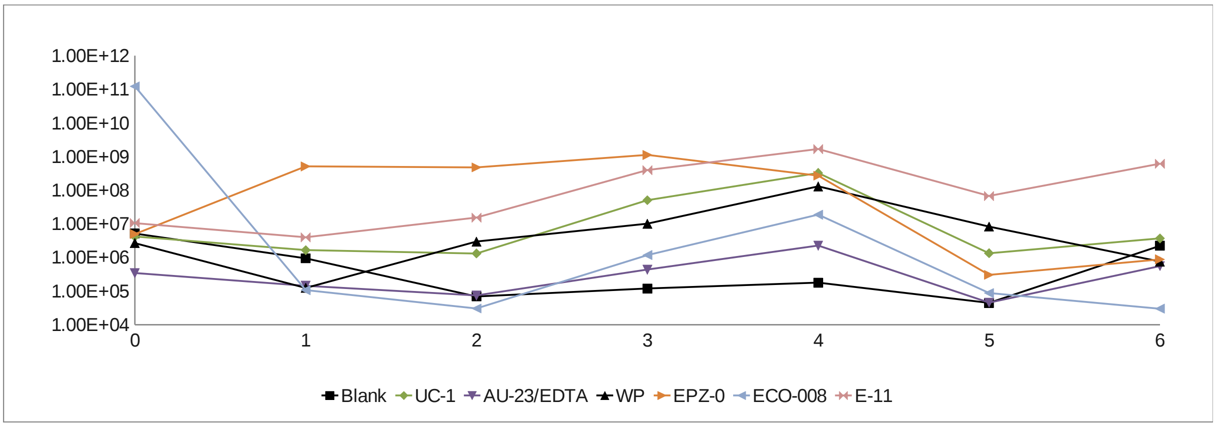


Figure 41b

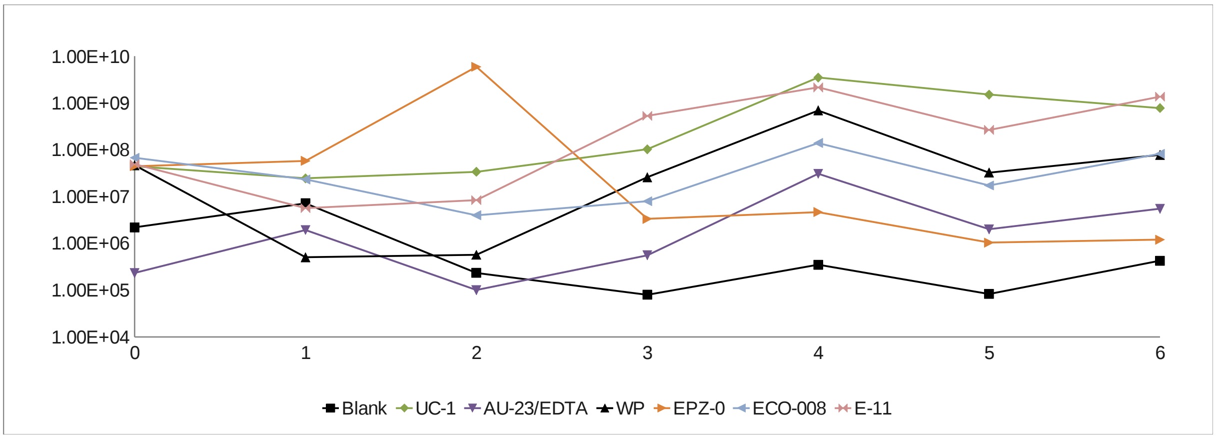


Figure 41c

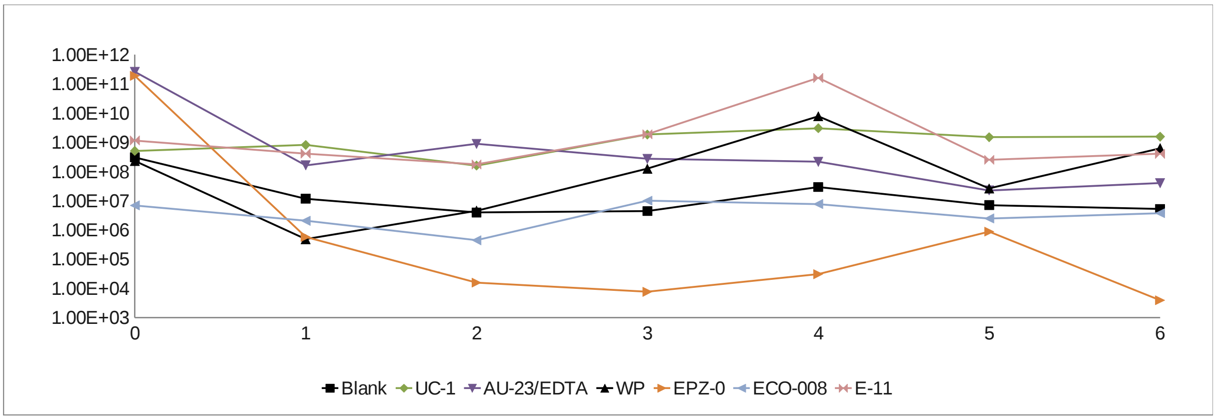


Figure 41d. Low-frequency (10^{-2} Hz) modulus vs. exposure time of primed and topcoated CRS panels continuously exposed to 5% NaCl solution; various candidate wash primers were tested, including DoD-P-15328D, EPZ, E-11, UC-1 Superprimer, AU-23, ECO-008 and an untreated control; the primers were: a) MIL-PRF-53022C, b) MIL-DTL-53030B, c) MIL-PRF-85582D, d) MIL-PRF-23377J; the topcoat was MIL-C-53039A.

These results did not correlate with other test results, such as SST or CCT. Further, the rather strong fluctuations that were observed suggested that the topcoat dominated the results and should be omitted. Thus, new panels were prepared which were pretreated and primed only. Care was taken to keep the primer thickness as constant as possible within a series of test panels.

These non-scribed test panels were then exposed in the GM9540P test along with regular scribed panels. In several other tests, a scribe was actually made in one half of the panel and the other half was reserved for the EIS measurement. In this way, a better comparison between the behavior in the scribe and the coating degradation, as measured by EIS, could be made. The EIS data were collected once a week, using an electrolyte of only 0.5% NaCl, in order to minimize corrosion effects during the measurements.

It should be realized that even with these modifications a one-to-one correlation between EIS and either SST or CCT can still not be expected. EIS measures degradation of intact coatings when exposed to an electrolyte environment. Such degradation can result from degradation of the coating, but also of the metal pretreatment, i.e., the stability of the coating-metal interface is an important factor. This degradation does not necessarily include corrosion reactions, at least not initially. Thus, one can expect a better correlation between EIS results and outdoor exposure, although in the latter situation UV light may play a role, which is absent in EIS, obviously. Thus, an EIS result of a metal/pretreatment/coating system is another piece of important performance information. An ideal system needs to perform well in SST, in CCT, in outdoor exposure, and in EIS.

Several EIS experiments were conducted using the improved procedure. Typically, an EIS experiment was conducted for 7 weeks, or about 1000 hours, which is also the length of time of an SST or CCT experiment of scribed panels. In the following, results of the low-frequency (10 mHz) impedance modulus of the system vs. time, are shown, which is a common procedure. The assumption here is that the higher that modulus or the more stable it is over time, the better the system will perform in the field in situations where there is no mechanical

damage to the coating and where UV radiation cannot skew the results. A decrease in impedance implies an increased absorption of electrolyte by the coating. A very thin metal pretreatment, such as the ones we are testing here, can affect the overall stability of the entire coating system if it is the only variable in the system, i.e., when the coating system is kept constant.

No attempts have been made to fit the EIS data to models which would be based on the so-called Equivalent Circuit Modeling approach idea. Such models would have yielded quantitative values for the various electrochemical components of the system. Since this project was one of optimizing performance of a new treatment and not a scientific project, it was felt that such a data analysis was not relevant in this project.

Experiment no. 1: Test of non-rinsed ECO-008 films on CRS – As discussed earlier in the text, the non-rinse (dry-in-place) version was one of the modifications implemented for process simplification. The EIS test was performed in order to investigate whether the non-rinsed film can form a stable interface with a WB or SB military primer using CRS as the substrate. The results are shown in Figure 42 for both primers. In this and all other cases where these primers were used, they were cured at RT for 14 days after HVLP spraying. Unless noted otherwise, the wash primers were always dried for 30 min. at RT prior to priming.

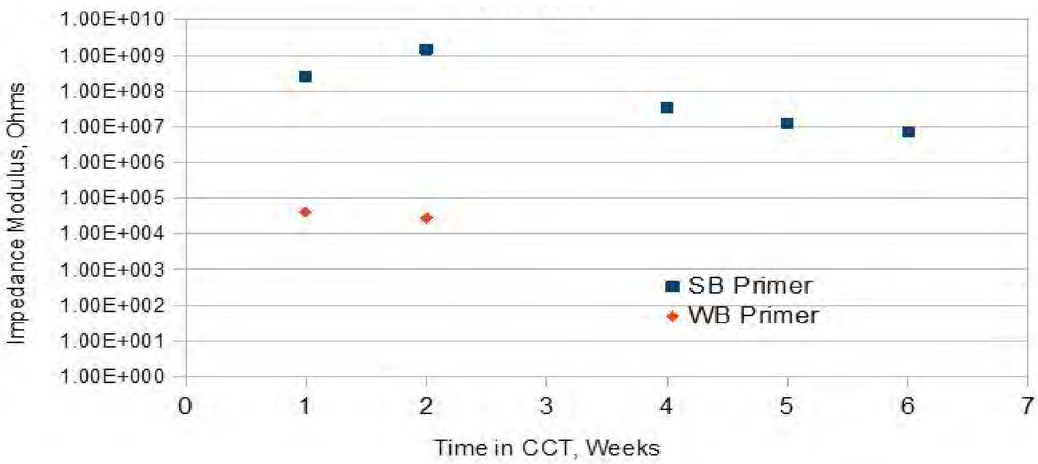


Figure 42. Low-frequency (10^{-2} Hz) modulus vs. exposure time in the CCT GM9540P test of primed CRS pretreated with ECO-008 that was dried in-place, i.e., not rinsed after HVLP spraying; WB = water-borne primer MIL-P-53030C; SB = solvent-borne primer MIL-P-53022D; both are chromate-free; total thickness was around 2 mil (50 µm); EIS in 0.5% aerated NaCl solution; the AC amplitude in all EIS data was 50 mV.

In this and subsequent figures the range of the modulus shown is always from 1 to 10^{10} Ω. That facilitates comparison between systems. A good primer system for CRS has an initial (and stable) low-frequency modulus of no less than 10^9 Ω. Coated metals with lower modulus will fail early in EIS, SST and CCT tests. With the WB primer a modulus higher than 10^6 Ω was never observed, so it is inherently a poor system that cannot perform well in the SST and CCT tests. The coating is too permeable to the electrolyte. It is hydrophilic, typical of WB systems. Yet, it is interesting to use it and see how much the pretreatment can improve its performance. The real performance of a pretreatment that ECOSIL would like to promote as a

replacement for the DoD-P-15328D wash primer, can only be judged from its performance under the SB primer, however.

It is seen in Figure 42 that the SB-primed system barely reaches 10^9 Ω and then drops off with time. Thus, it is a reasonable, but not outstanding system. The WB-primed system did not even reach 10^5 Ω, so it was poor. The test with the WB primer was discontinued after 2 weeks of exposure, as rust breaking through the coating became visible at that time.

Experiment No. 2: Test of initial set of candidate wash primers – Figures 43-46 show the EIS results for various candidate primers discussed in the previous sections, as well as for the commercial WP and untreated controls. The primers were applied on CRS and AA7075-T6. The same primers were used as those of Figure 42.

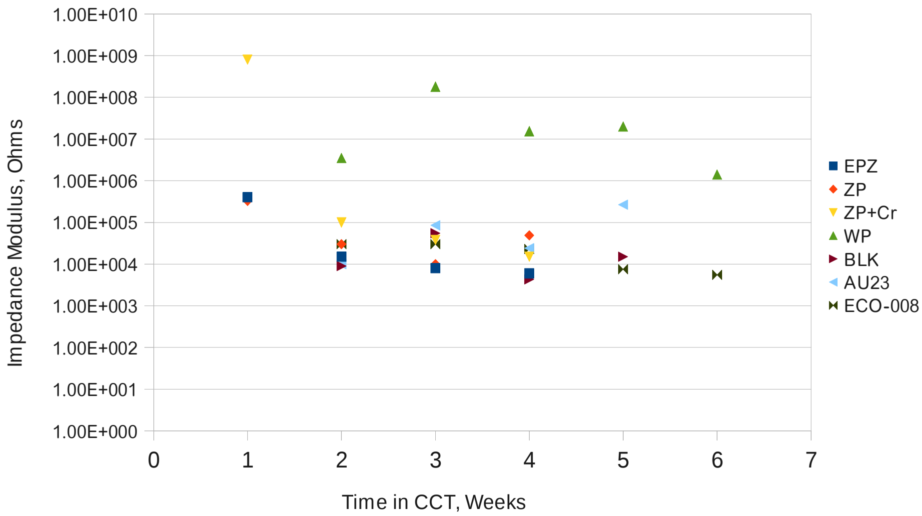


Figure 43. Low-frequency (10^{-2} Hz) modulus vs. exposure time in the CCT GM9540P test of primed CRS pretreated with the candidate wash primers EPZ, AU23 and ECO-008; zinc phosphate (ZP) and Cr(VI)-sealed zinc phosphate (ZP+Cr) were used as controls; other controls were the commercial wash primer DoD-P-15328D (WP) and an untreated panel (BLK). The water-borne primer was MIL-P-53030C.

These results show that in this experiment only the commercial wash primer was capable of giving a sustained modulus higher than 10^6 Ω. Even the ZP+Cr system, known to be the best metal pretreatment in the business, dropped quickly to around 10^4 Ω, along with all our candidate primers.

Figure 44 shows the results for the same experiment but now using the SB primer MIL-P-53022D. In this case a different trend is observed. First, the candidate AU23 performs very poorly, in agreement with its SST and CCT performance. All others are very similar and hover around the 10^9 Ω line, indicating good performance levels, although there is a tendency for a slow decrease with time, as is normal for coated systems.

The results obtained with the WB primer on AA7075-T6 are shown in Figure 45. All values are rather low, but very stable with ECO-008 showing the highest values. Even the untreated control (BLK) performs relatively well.

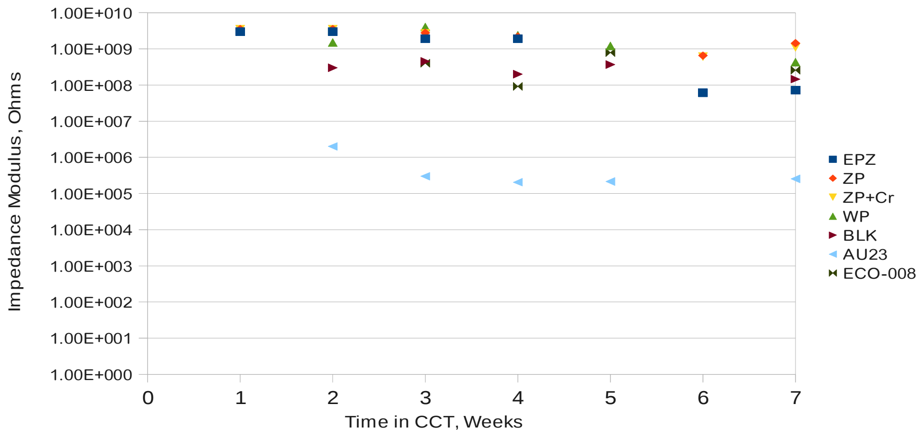


Figure 44. Low-frequency (10^{-2} Hz) modulus vs. exposure time in the CCT GM9540P test of primed CRS pretreated with the candidate wash primers EPZ, AU23 and ECO-008; zinc phosphate (ZP) and Cr(VI)-sealed zinc phosphate (ZP+Cr) were used as controls; other controls were the commercial wash primer DoD-P-15328D (WP) and an untreated panel (BLK). The solvent-borne primer was MIL-P-53022D.

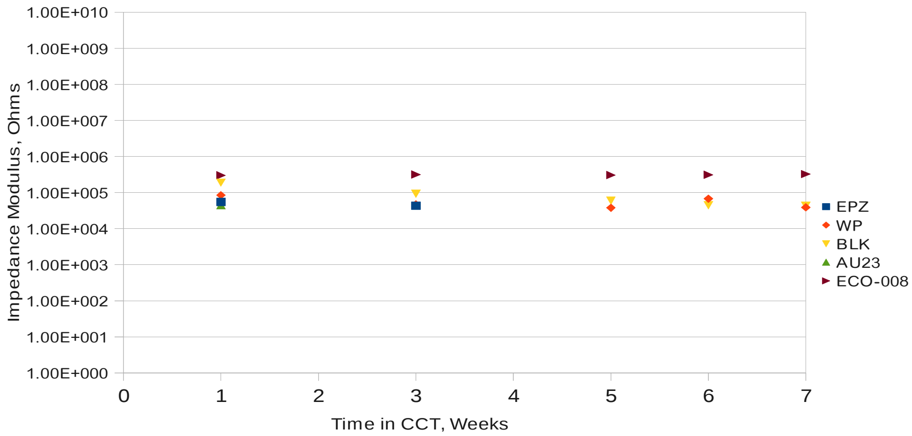


Figure 45. Low-frequency (10^{-2} Hz) modulus vs. exposure time in the CCT GM9540P test of primed AA7075-T6 pretreated with the candidate wash primers EPZ, AU23 and ECO-008; controls in this case were the commercial wash primer DoD-P-15328D (WP) and an untreated panel (BLK). The water-borne primer was MIL-P-53030C.

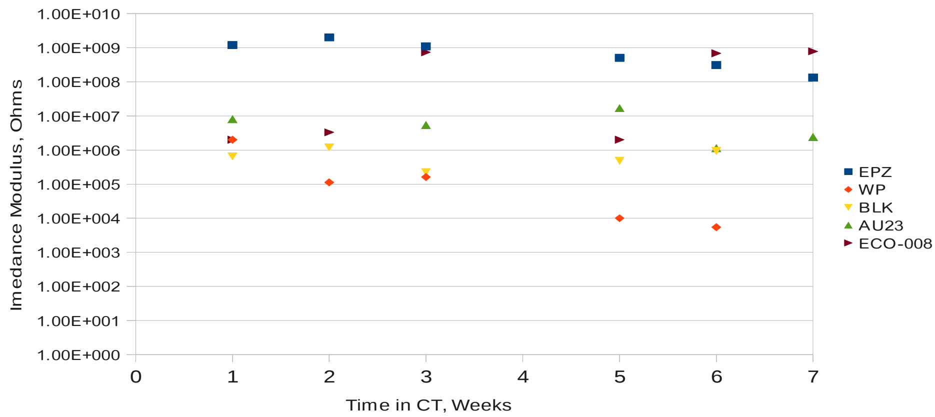


Figure 46. Low-frequency (10^{-2} Hz) modulus vs. exposure time in the CCT GM9540P test of primed AA7075-T6 pretreated with the candidate wash primers EPZ, AU23 and ECO-008; controls in this case were the commercial wash primer DoD-P-15328D (WP) and an untreated panel (BLK). The solvent-borne primer was DoD-P-53033C.

Figure 46 shows the results for the solvent-based primer on this metal. The trend here is different. The commercial WP performs remarkably poorly here. It is worse than the untreated control. Clearly, the best performers here are EPZ and ECO-008.

After the tests of Figures 43-46 were completed, the residual adhesion of the primer to the metal was determined, using the standard ASTM D3359 test. Panels that did not make it through the 6-week exposure were not included. The results are shown in Table 37. It is seen that the only two CRS/WB systems that made it through 6 weeks in the exposure test (Figure 42) had 0B adhesion, i.e., were very poor. For AA7075-T6, three systems made it through 7 weeks (Figure 45). Their residual adhesion was poor for the WP but very good (5B) for ECO-008. The untreated control BLK had 3B.

For both CRS and AA7075-T6 all SB systems made it through 7 weeks. For CRS the two phosphated systems did very well (5B) and so did the WP and the ECOSIL systems ECO-008 and EPZ. The control and AU 23 were poor. On AA7075-T6 the DoD-P-15328D wash primer was remarkably poor. All others, including the control BLK did very well.

The combined EIS and adhesion results contributed to the decision to drop further development of EPZ and AU23 and to focus instead on the further improvement of ECO-008, especially under the WB primer. As a conclusion of the EIS data presented so far, it seems that the Cr(VI)-free, low-VOC system ECO-008 can favorably compete with the commercial wash primer, except on CRS under the WB primer. As discussed earlier in this report, some of the improvements that were tested included the no-rinse version and the addition of resins.

Experiment No. 3: Test of ECO-008 with resin addition – ECO5-1 and ECO5-5 were tested on CRS under the SB military primer and compared with the unmodified ECO-008 system. The results are shown in Figure 47. More systems were actually tested in this experiment, but they failed because of a high porosity of the primers. That was due to a spray error. The ones shown here were not porous. The systems were *not* rinsed. So the results should be compared to those of Figure 42.

Table 37. Adhesion of samples of Figures 41-44 after 7-week GM9540P exposure

System	Adhesion
CRS – WB – DoD-P-15328D	0B
CRS – WB – ECO-008	0B
CRS – SB – DoD-P-15328D	4B
CRS – SB – ECO-008	4B
CRS – SB – AU23	1B
CRS – SB – EPZ	5B
CRS – SB – ZP	5B
CRS – SB – ZP + Cr	5B
CRS – SB – BLK	0B
Al – WB – DoD-P-15328D	1B

Al – WB – ECO-008	5B
Al – WB – BLK	3B
Al – SB – DoD-P-15328D	0B
Al – SB – ECO-008	5B
Al – SB – AU23	5B
Al – SB – EPZ	5B
Al – SB – BLK	5B

It is observed here that, for the first time, the modulus remains at the 10^9 Ω or higher level over the entire 7-week period for the resin-modified systems. The unmodified ECO-08 begins to fail and drop off after about 5 weeks, as observed before. Thus, the resin addition significantly improves the ECO-008 system. In Table 38 the residual adhesion of the samples of Figure 47 are shown.

Table 38. Adhesion of ECO-008/resin systems of Figure 46 after 7-week GM9540P

System	Adhesion
ECO5-1 (Resin 5-1)	5B
ECO5-5 (Resin 5-5)	4B
ECO-008	1B

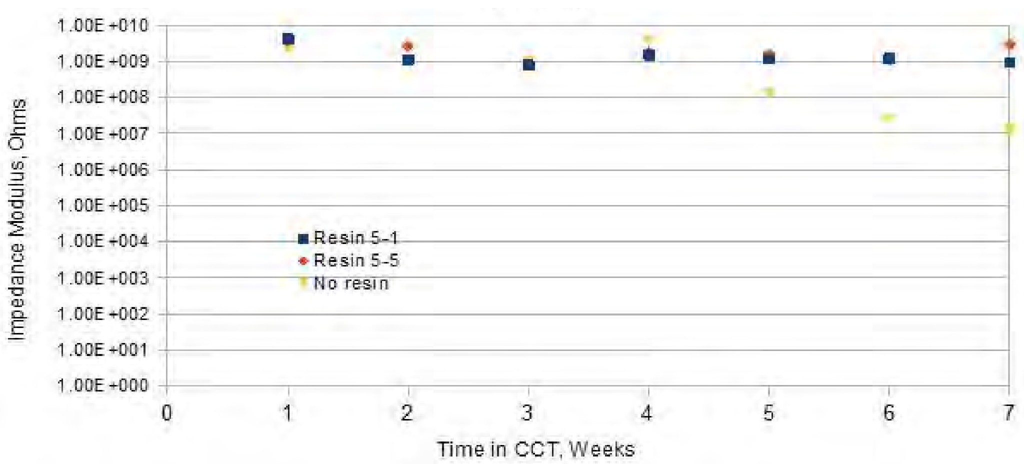


Figure 47. Low-frequency (10^{-2} Hz) modulus vs. exposure time in the CCT GM9540P test of primed CRS pretreated with ECO-008 and resin modifications 5-1 and 5-5 of Table 21. The solvent-borne primer was MIL-P-53022D.

It is seen that the resin addition also significantly improves the adhesion after the test. The obvious next step was then to repeat these results and compare them directly with those of the DoD-P-15328D wash primer using both primers and substrates used before.

Experiment No. 4: EIS of ECO5-1 and ECO5-2 on CRS and AA7075-T6 under both primers – The results of this experiment are shown in Figures 48 and 49. Resin modifications 5-1 and 5-2 were selected as they had performed best in the SST and CCT tests.

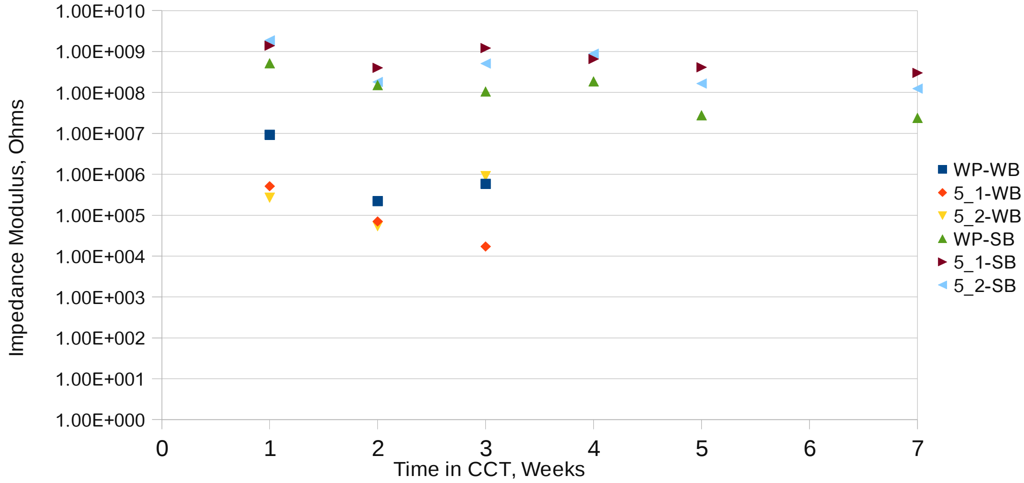


Figure 48. Low-frequency (10^{-2} Hz) modulus vs. exposure time in the CCT GM9540P test of primed CRS pretreated with resin modifications 5-1 and 5-2 of Table 21 and the commercial DoD-P-15328D wash primer. The solvent-borne primer was MIL-P-53022D, the water-borne primer was MIL-P-53030C. The test was ended after 7 weeks (49 cycles).

These preliminary results are encouraging as they indicate an excellent performance of the resin-modified ECO-008 for use under the SB primer. The values are consistently higher than for the DoD-P-15328D wash primer and are at the 10^9 Ω level. For the WB primer, the results were less impressive. After three weeks all systems, including the DoD-P-15328D wash primer, were withdrawn because of visible rust formation. Nonetheless, the resin-modified ECO-008, especially 5-2, is equivalent in performance to the commercial WP system.

The residual adhesion (at the end of the test) was 5B for the three solvent-borne systems and 0B for the three water-borne systems. Here, too, the performance of the resin-modified ECO-008 system is at least equivalent to that of the DoD-P-15328D.

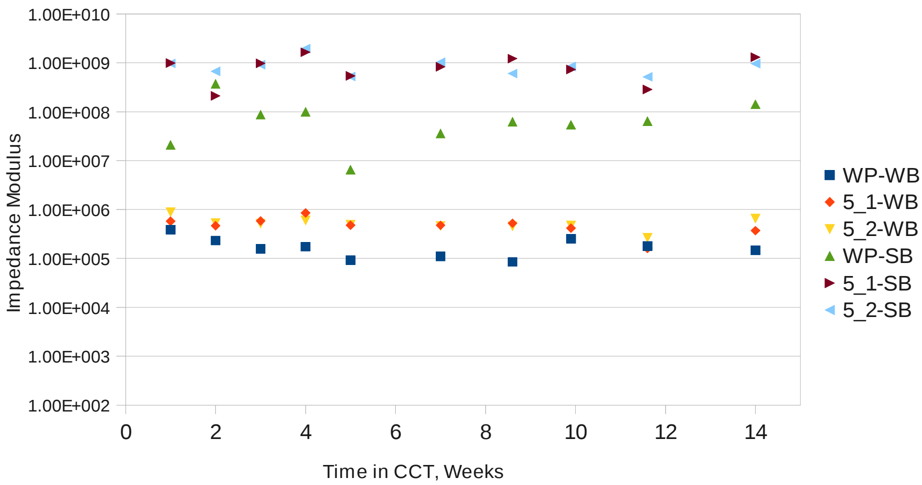


Figure 49. Low-frequency (10^{-2} Hz) modulus vs. 96 cycles exposure time in the CCT GM9540P test of primed AA7075-T6 pretreated with resin modifications 5-1 and 5-2 of Table 21 and the commercial DoD-P-15328D wash primer. The solvent-borne primer was MIL-P-53022D, the water-borne primer was MIL-P-53030C.

For the aluminum alloy, shown in Figure 49, the results in terms of performance are similar to

those obtained with CRS. Under the SB primer both resin-modified ECO-008 systems perform better than the DoD-P-15328D wash primer and are above the 10^9 Ω level. The WB systems are quite constant and both are very close to the 10^6 Ω level. Both resin-modified ECO-008 systems are markedly higher than the DoD-P-15328D wash primer, at least up until 9 weeks.

In Table 39 the residual adhesion after 96 cycles of the GM9540P test is shown.

Table 39. Adhesion of ECO-008/resin systems of Figure 49 after 14-week GM9540P

System	Adhesion
ECO5-1 (Resin 5-1) – WB	5B
ECO5-5 (Resin 5-5) – WB	4B
DoD-P-15328D – WB	0B
ECO5-1 (Resin 5-1) – SB	5B
ECO5-5 (Resin 5-5) – SB	5B
DoD-P-15328D – SB	5B

It can be concluded that all samples have retained their excellent throughout the exposure period, with the exception of the DoD-P-15328D wash primer coated with the water-borne primer, which has dropped to a 0B (complete delamination) level. Again, the DoD-15328D primer does not work too well on Al alloys, especially under a WB primer. This may be caused by the lack of etching of the substrate by the phosphoric acid in the wash primer. CRS is etched more readily than an Al alloy by phosphoric acid. The excellent adhesion of the resin-modified ECO-008 system under both primers is again confirmed. This system does not rely on substrate etching, but adhesion here is obtained through the use of the silane.

5.2.5. FTIR characterization

FTIR spectra of DoD-P-15328D, ECO-008 and ECO5-1 are shown in Figures 50-52. The FTIR spectrum of the DoD-P-15328D wash primer is shown in Figure 50. This is just for reference and cannot be compared with any ECOSIL system because of a different resin type. The DoD-P-15328D wash primer is based on polyvinylbutyral (PVB) resin and ECO5-1 is based on an epoxy resin.

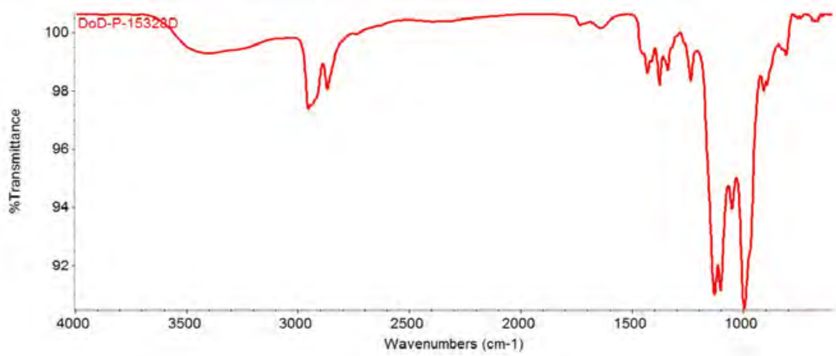


Figure 50. FTIR spectrum of DoD-P-15328D wash primer.

Figure 51 shows the change of modification of ECO-008 (top, in red) to ECO5-1(bottom, in blue). With the introduction of the epoxy resin, the peaks of the Si-O-Si group at around 1000 cm^{-1} (1118 cm^{-1} and 1037 cm^{-1}), which are Si-O asymmetric stretching bands) are suppressed by organic groups in the epoxy resin.

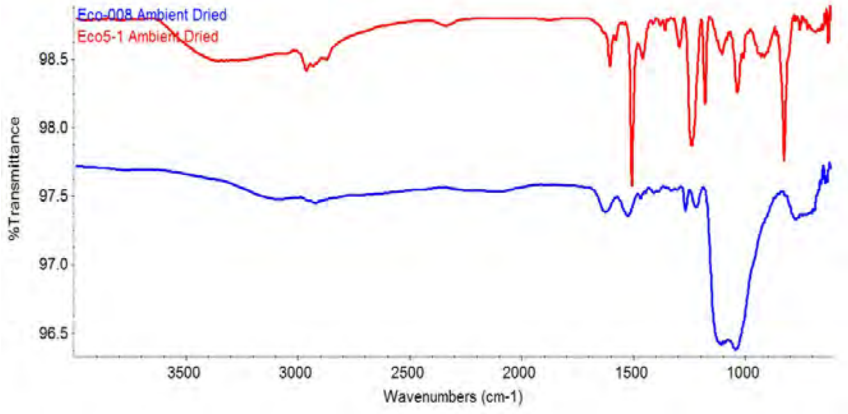


Figure 51. FTIR spectra of ECO-008 and ECO5-1.

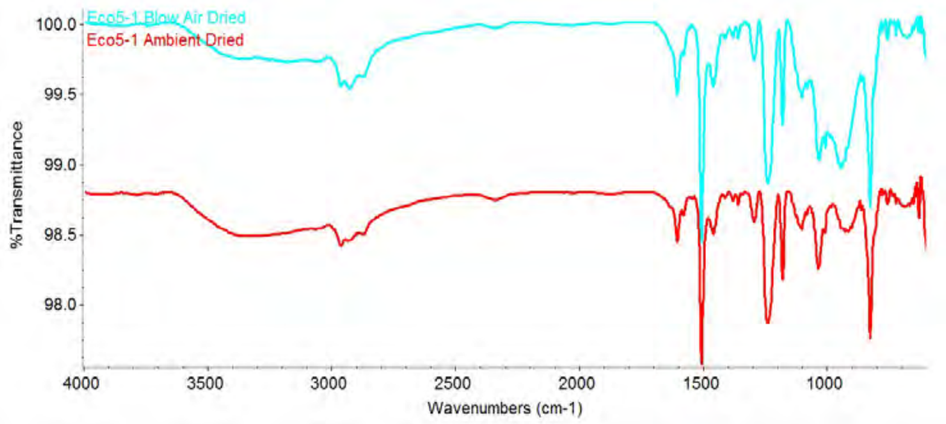


Figure 52. FTIR spectra of ECO5-1with different drying conditions.

Different drying conditions of ECO5-1 were tested for performance changes (see section 3.3.2.3). The spectra of ECO5-1 ambient dried (Figure 52, bottom, in red) and hot-air-dried ECO5-1(top, in green) are almost identical. The only slight difference is a difference in the -OH band in the 3000-3500 cm^{-1} region, which is due to water in the film. This band is lower in the hot-air dried film.

5.3 Conclusions

The new wash primer system that is proposed as a result of the R&D in this SERDP project is the ECO5-1 system, which is the non-rinse resin-modified ECO-008 system. It is water-based, has almost no VOC, contains no HAPs and is devoid of chromate, which was the major aim of the project. The system is easily applied by HVLP spraying and can be primed after 30 min. drying at RT. It has superior adhesion properties and works well on CRS and AA7075-T6. This system has not yet been exposed at the Florida exposure site, but all indications are that it will perform there, too, as its precursor ECO-008 (i.e., without resin) has performed well in the first 6 months of Florida exposure.

The system is easy to prepare and is considerably thinner than the currently used DoD-P-15328D wash primer. This can be construed as an additional advantage, as it will save costs. Despite the low coating weight, the system works well on marginally prepared surfaces, e.g., sandpaper-roughened surfaces. The surface preparation is not critical.

The new wash primer performs well and is at least equal to and often better than the commercial wash primer DoD-P-15328D for CRS. On AA7075-T6 the new system performs markedly better than the DoD-P-15328D wash primer. Such performance was noted in EIS, SST, CCT and CASS test conditions. Adhesion and impact resistance are superior to those of DoD-P-15328D wash primers.

5.4 References

1. http://www.serdp.org/Program-Areas/Weapons-Systems-and-Platforms/Surface-Engineering-and-Structural-Materials/Coatings/WP-1341

Appendix A. Results under a Chromate-free, low-VOC, Water-borne Epoxy Primer

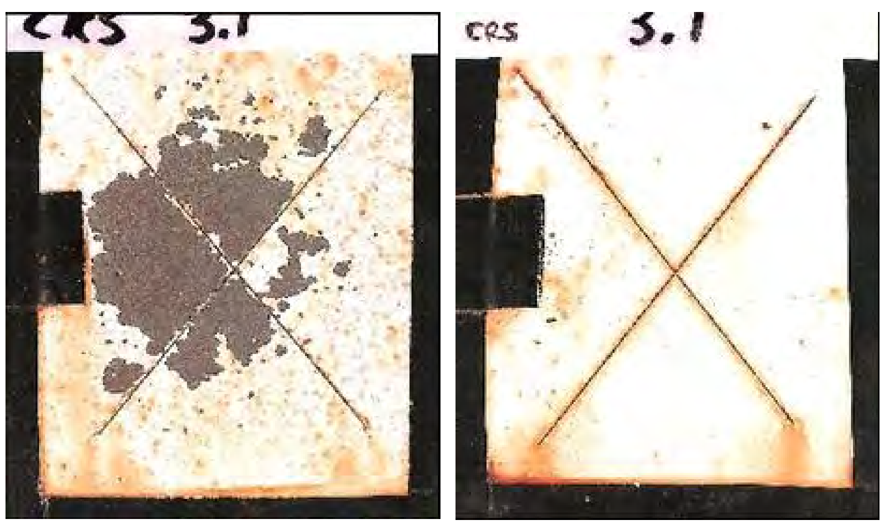
A-1. Background

A chromate-free, low-VOC water-borne epoxy primer with code name E-11 was evaluated and optimized early on in this project as a candidate green wash primer to replace the DoD-P-15328D wash primer (see Section 2 for the details). The test results indicated that E-11 is not good enough to be used as an effective replacement for DoD-P-15328D. Later in the project E-11 was tested on pretreated CRS again, but now as a green water-borne epoxy *primer* of regular primer thickness of around 25 µm. It was compared with the current water-borne military epoxy primer MIL-P-53030C, which has been shown in this project to posses poor corrosion-protection properties. In the following some data are reported which confirm that E-11 is an effective primer in its own right.

A-2. Corrosion testing

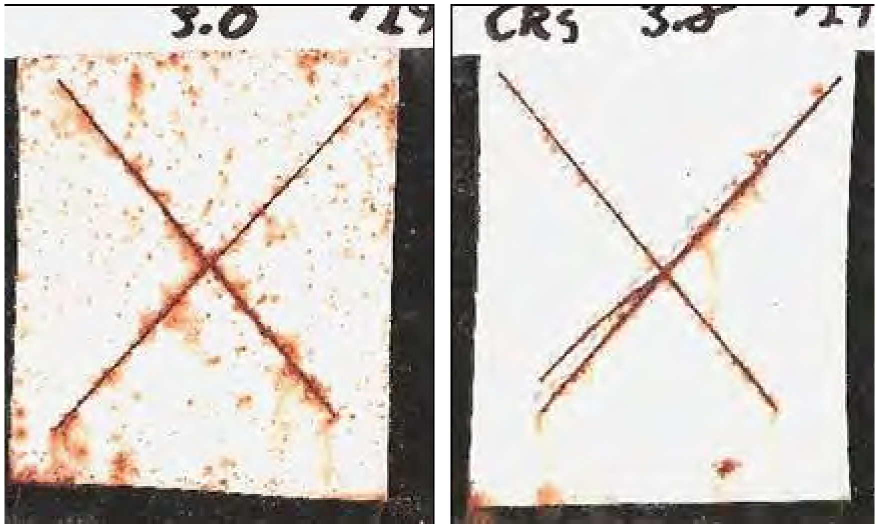
Pretreated CRS samples that were tested included: (1) CRS pretreated with DoD-P-15328D, (2) CRS pretreated with ECO5-1 and, (3) zinc-phosphated CRS. It should be noted that (1) and (2) were prepared at ECOSIL while samples of (3) were purchased from ACT Test Panels, Inc. Sandpaper roughening with #150 sandpaper and steel shot blasting were used as surface preparation methods, prior to the application of the wash primers.

The corrosion tests used were: (1) the neutral salt spray test (ASTM B117); and, (2) the cyclic corrosion test GM 9540P. The test results are shown in Figures 53-57.



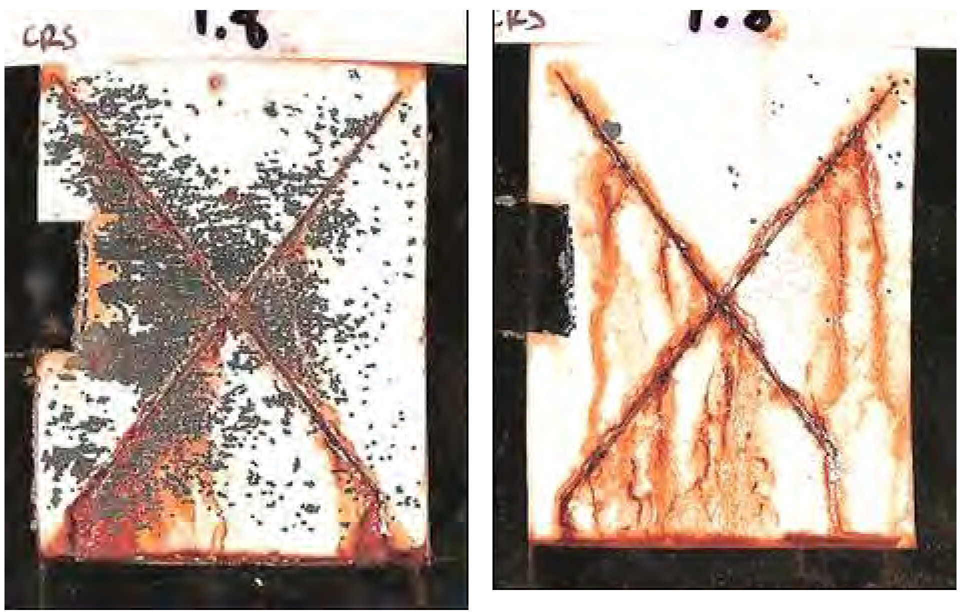
(a) (b)

Figure 53. 240-hr SST result for CRS first treated with DoD-15328D, and followed by (a) MIL-P-53030C, and (b) E-11; surface preparation: sandpaper roughening.



(a) (b)

Figure 54. 30-cycle CCT result for CRS first treated with DoD-15328D, and followed by (a) MIL-P-53030C, and (b) E-11; surface preparation: sandpaper roughening.

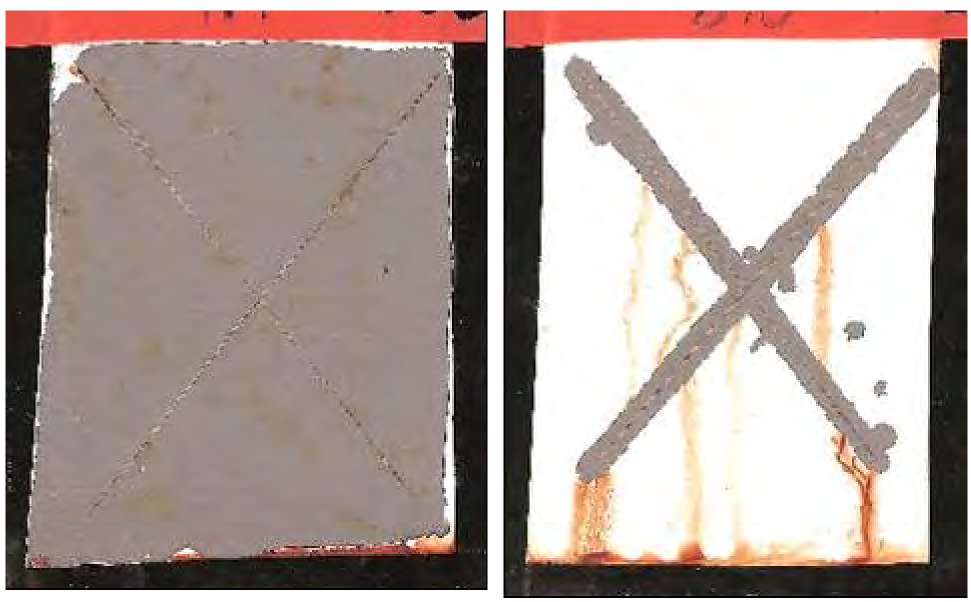


(a) (b)

Figure 55. 240-hr SST result for CRS first treated with ECO5-1, and followed by (a) MIL-P-53030C, and (b) E-11; surface preparation: sandpaper polishing.

(a) (b)

Figure 56. 30-cycle CCT result for CRS first primed with ECO-5-1, and followed by (a) MIL-P-53030C, and (b) E-11; surface preparation: sandpaper roughening.



(a) (b)

Figure 57. 240-hr SST result for Zn-phosphated CRS with (a) MIL-P-53030C, and (b) E-11; surface preparation: sandpaper roughening.

The results show that in all cases, i.e., SST and CCT test and for both the DoD-P-15328D wash primer and ECO-5-1, rust spots are already breaking through the coating in the case of the primer MIL-P-53030C, but not in the case of the E-11 primer. In the SST, part of the primer has delaminated, both for the DoD-P-15328D wash primer and for ECO5-1. Such delamination is not observed for the E-11 primer.

A striking result is seen in Figure 57 for the system consisting of the MIL-P-53030C primer on zinc phosphated CRS. After 240 hours SST, the entire primer coating has delaminated. This is an adhesion issue, not a corrosion problem, as there is little or no rust visible under the primer. With E-11, there is only 2 mm delamination along the scribe lines. It can be speculated that since the primer MIL-P-53030C is so permeable to electrolyte (as was concluded from the EIS data in section 5 and from section A-3 below), it will swell in electrolyte causing shear stresses to develop along the interface. The primer can then lose its adhesion. If the primer is much less permeable, such as in the case of E-11, it will not develop such shear stresses and adhesion is maintained.

It can be concluded from these Figures that the current water-borne military primer, MIL-P-53530C, has two major performance issues. First, MIL-P-53030C is highly permeable to water penetration which results in severe blistering in both SST and CCT tests. Secondly, it is often observed that premature intercoat adhesion failure between MIL-P-53030C and DoD-P-15328D occurs, e.g., in Figure 53(a). This suggests that MIL-P-53030C somehow is not compatible with DoD-P-15328D. E-11 does not show these weaknesses. It has more water resistance and very good compatibility with the DoD-P-15328D wash primer.

A-3. EIS measurements

Samples of CRS coated with the WB primer MIL-P-53030C and with the ECOSIL E-11 primer were tested by EIS. Care was taken to deposit approximately the same coating thickness of both primers. They were both cured at RT for 2 weeks. These measurements are still in progress, but initial data in terms of low-frequency impedance are reported here. Table 40 shows the low-frequency impedance recorded after 13 days in the CCT chamber.

Table 40. Impedance values of coated CRS under MIL-P-53030C and E-11*

System	Pretreatment	Primer	Impedance	Comments
ZP-1	Zinc Phosphate	MIL-P-53030C	123 kΩ	Rust spots in coating
ZP-2	Zinc Phosphate	E-11	20.4 MΩ	No rust spots
EC-1	ECO-008	MIL-P-53030C	9.9 MΩ	Rust spots in coating
EC-2	ECO-008	E-11	35.6 MΩ	No rust spots
ZPCr-1	Zinc Phosphate/Cr(VI)	MIL-P-53030C	283 kΩ	No rust sports
ZPCr-2	Zinc Phosphate/Cr(VI)	E-11	40.0 MΩ	No rust spots

*after 13 days in the CCT test

These data show that the E-11 coating has a much higher impedance than MIL-P-53030C, which implies that it has greater resistance to penetrating electrolyte (barrier action). This impedance is of the order of 10^7 Ω. In section 5 it was argued that a good WB coating needs an impedance of at least 10^6 Ω for performance. Thus, the E-11 primer has an even higher impedance than this minimum value. The lower permeability of this

primer is also confirmed by the comments in the last column: the coatings of MIL-P-53030C already show rust spots breaking through the coating in the case of zinc phosphate and ECO-008 pretreatments. Such spot are absent in the case of the E-11 coating.

The data in the table further show that the MIL-P-53030C system with ECO-008 pretreatment, the basis for the new wash primer ECO5-1, has a considerably higher impedance than the ones with zinc phosphate and Cr(VI)-sealed zinc phosphate. This observation explains why the SST and CCT results discussed above were so favorable. The combination ECO-008/E-11 or, in the case of wash primers, ECO5-1/E-11 appears to be a very powerful, water-borne, chromate-free combination.

A-4. Conclusions

The overall result of this project is that a new water-borne, chromate-free wash primer has been developed that performs particularly well in combination with a new water-borne primer, which is also chromate-free. This combination performs better in both SST and CCT tests than the current combination of the DoD-P-15328D wash primer and the MIL-P-53030C water-borne primer. Its performance also rivals that of the combination of the wash primer DoD-P-15328D with the SB primer MIL-P-53022D, which is often used. Thus this project had no only led to the elimination of chromate in the wash primer, but also to the potential elimination of the solvent in the primer that needs to be used over the wash primer. The new combination has been successfully tested on CRS and AA7075-T6 substrates.

Appendix B. Results of Recent Performance Tests with ECO5-1 not included in the Draft Report

The final wash primer ECO5-1 of Section 3 was tested in several experiments in order to verify its reproducibility and its dependence on the cleaning procedure prior to the wash primer application. CRS and AA7075-T6 were used as substrates in the experiments of this section.

B-1. Effect of metal cleaning prior to primer deposition

a) EIS data

In this experiment the metal preparation prior to the wash primer application was investigated and compared. Also, new batches of MIL-P-53030C and MIL-P-53022D WB and SB primer were used, manufactured by DEFT Finishes Inc. and supplied by D&S Color Supply Inc. The preparation methods were:

1. Acetone wipe, roughening with #150 sandpaper, followed by city water rinsing
2. Alkaline cleaning, followed by CW rinsing
3. Acetone degreasing, shot-blasting with 70-grit steel shot for 60-90 s, followed by CW rinsing; this treatment was only applied to CRS, not to AA7075-T6.

Methods No. 1 and 3 are practical surface preparation methods that could be used in the field, e.g., in repair procedures. For CRS all three methods were used, for AA7075-T6 only methods 1 and 2. The DoD-P-15328D wash primer and an untreated panel were used as controls. They were applied over the shot-blasted substrate (for CRS) or alkaline-cleaned by method No. 2 (for Al). The tests performed with these panels were EIS, GM9540P, SST and CASS. EIS and CCT were done on two sections of the same panel.

Figures 58 and 59 shows the EIS data for the CRS and AA7075-T6 panels. CRS was subjected to 52 cycles, the aluminum alloy to 80 cycles in the GM9540P test. AA7075-T6 was tested with the SB primer only.

We can conclude from these data that, at least in this test, the ECO5-1 system performs on par with the DoD-P-15328D wash primer under the SB primer, both on CRS and on AA7075-T6. For all systems the impedance modulus does not change much over the period of the test. Under the WB primer, which is much more permeable and hydrophilic than the SB primer, there was a slow decrease of impedance, as expected, but the trend is again similar for all systems. Another conclusion from the data is that the method of pretreatment of the substrate is irrelevant. All three pretreatment methods perform approximately the same. This is of great importance for the use of the new wash primer in difficult field conditions, where alkaline cleaning or shot-blasting is not possible and sandpaper roughening may be the only resort.

The residual adhesion after the CCT/EIS test was determined using the ASTM D3359 crosshatch and tape-pull test. The results are shown in Table 41. These results show that the new wash

primer has a residual adhesion that is superior to that of the current DoD-P-15328D wash primer to both metals, despite the absence of the phosphoric acid in the system. That acid is thought to be the component that causes the DoD-P-15328D wash primer to adhere well to steel through an etching effect.

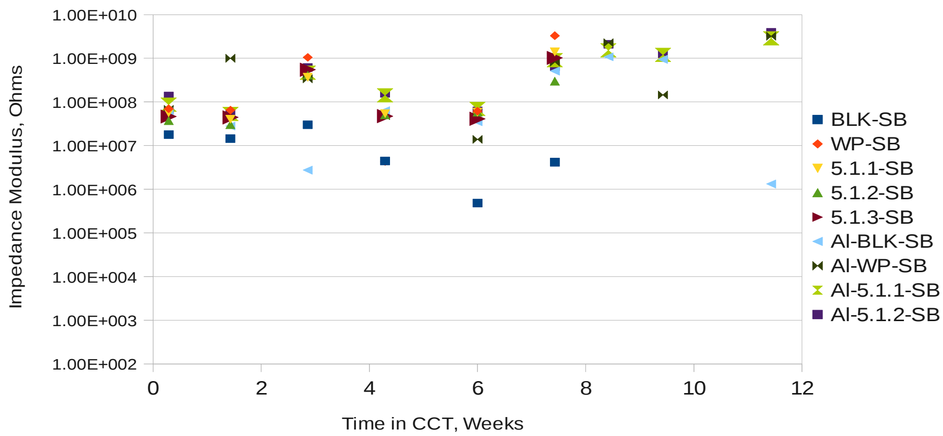


Figure 58. Low-frequency (10^{-2} Hz) modulus vs. 52 or 80 cycles exposure time in the CCT GM9540P test of primed CRS and AA7075-T6; the wash primer was the resin modification 5.1 of Table 21 (ECO5-1) and a commercial wash primer according to DoD-P-15328D; BLK is an untreated control; 5.1.1, 5.1.2 and 5.1.3 are different metal cleaning methods prior to the wash primer application, sandpaper roughening, alkaline cleaning and steel shot-blasting, respectively; the solvent-borne primer was MIL-P-53022D, the water-borne primer was MIL-P-53030C, both from DEFT. In this graph all SB systems are compared.

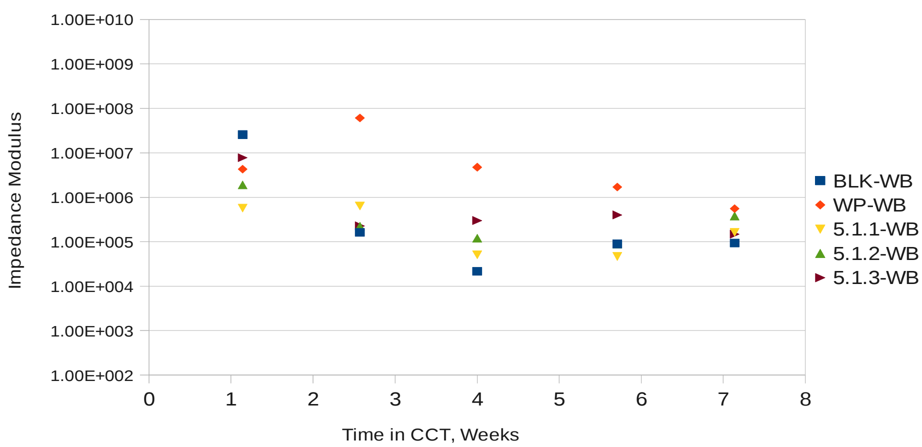


Figure 59. As in Figure 58, but shown here are the WB-primed CRS panels exposed for 52 cycles.

Table 41. Adhesion of ECO5-1 systems of Figures 58 and 59 after the GM9540P test

System	Adhesion
CRS-BLK-WB	0B
CRS-DoD-P-15328D-WB	2B
CRS-5.1.1-WB	5B

CRS-5.1.2-WB	5B
CRS-5.1.3-WB	5B
CRS-BLK-SB	4B
CRS-DoD-P-15328D-SB	3B
CRS-5.1.1-SB	5B
CRS-5.1.2-SB	5B
CRS-5.1.3-SB	4B

b) SST, CCT and CASS data

Test panels identical to those described in section a) were prepared and exposed in the SST and CCT tests. In this experiment the CASS test was also performed. The humidity chamber available at ECOSIL Technologies had been been modified so that this test could be carried out. It is essentially a salt spray test, but the salt solution now also contains also contains some copper sulfate and acetic acid (ASTM B-368-97, reapproved 2003). These additions make the solution much more aggressive toward aluminum alloys than the regular salt solution used in the B-117 test. The exposure time in the test of primed and scribed panels is, therefore, only 240 hours, as opposed to 2000 hours or longer for the regular B-117 test.

Figures 60 and 61 show the CRS panels after the SST test for the WB and SB primers that were used, respectively. Tables 42 and 43 show initial adhesion and impact data for these panels.

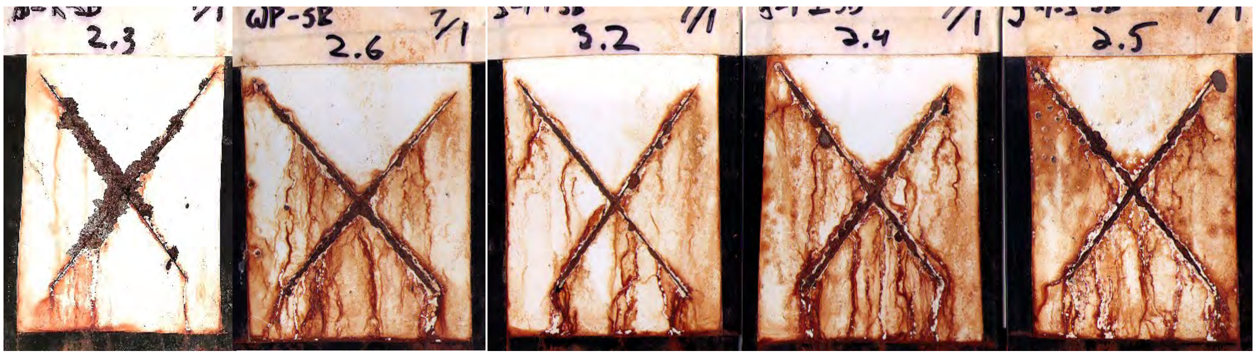
(a) (b) (c) (d) (e)

Figure 60. Primed CRS panels after 336 hours SST; the primer was Deft MIL-53030C (WB); (a) untreated control, steel shot-blasted; (b) DoD-P-15328D wash primer, steel shot-blasted; (c) ECO5-1 with sandpaper roughening (ECO5-1-1); (d) ECO5-1 on alkaline-cleaned panel (ECO5-1-2; (e) ECO5-1 on steel-shot-blasted panel (ECO5-1-3).

Table 42. Initial data for WB-primed CRS panels shown in Figure 60

Sample ID	DFT (mil)	Dry Adh	Wet Adh	Impact*
ECO5-1-1**	1.2	5B	5B	P
ECO5-1-2	1.3	5B	5B	P
ECO5-1-3	1.3	5B	5B	P
Untreated (S)	1.2	5B	4B	P
DoD-P-15328D	1.9	5B	4B	F

* Impact: 160 in-lb **Last digit is the metal cleaning process



(a) (b) (c) (d) (e)

Figure 61. Primed CRS panels after 1000 hours SST; the primer was Deft MIL-53022D (SB); (a) untreated control, steel-shot-blasted; (b) DoD-P-15328D wash primer, steel-shot-blasted; (c) ECO5-1 with sandpaper roughening (ECO5-1-1); (d) ECO5-1 on an alkaline-cleaned panel (ECO5-1-2); (e) ECO5-1 on a steel-shot-blasted panel (ECO5-1-3).

Several conclusions can be drawn from these data. The adhesion of the WB-primed systems is good. The impact resistance is good also, except for the DoD-P-15328D wash primer, which failed the test. The adhesion in the SB-primed systems is good for the ECO-5-1 systems and poor for the untreated control. The DoD-P-15328D wash primer is slightly worse than ECO5-1. All systems fail the 160 in-lb impact resistance test here. There are no differences between the three ECO5-1 systems, indicating again that the metal cleaning process is not an important factor.

Table 43. Initial data for SB-primed CRS panels shown in Figure 61

Sample ID	DFT (mil)	Dry Adh	Wet Adh	Impact*	SST (1000 hrs)**
ECO5-1-1***	2.4	4B	4B	F	1
ECO5-1-2	2.5	4B	4B	F	1.75
ECO5-1-3	3.2	4B	4B	F	1.75+Blister
Untreated	2.3	3B	1B	F	N/A
DoD-P-15328D	2.6	4B	4B	F	1.5

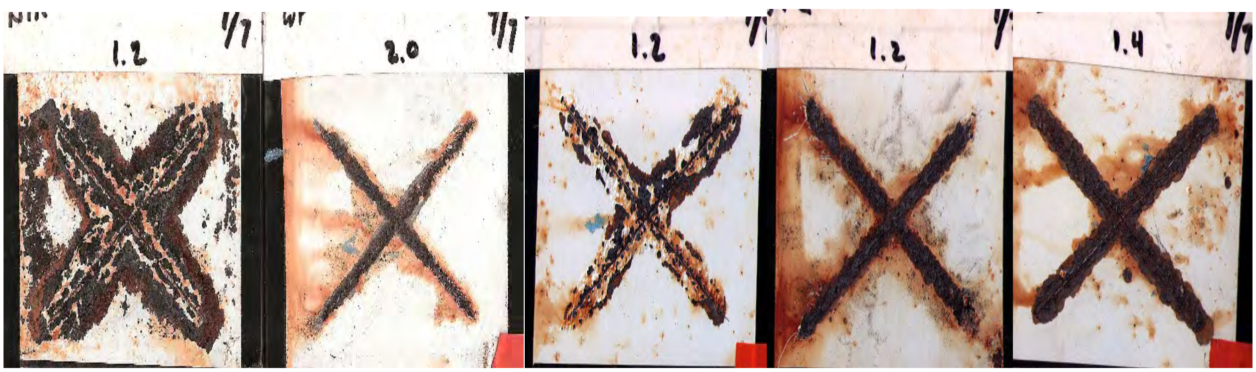
*Impact: 160 in-lb **mm creep ***Last digit is the metal cleaning process

The salt spray results indicate very little difference between the DoD-P-15328D wash primer and the ECO-5-1 systems. For the SB primer the performance is equivalent. For the WB primer the

creep is comparable, but the ECO5-1 systems show some small blisters.

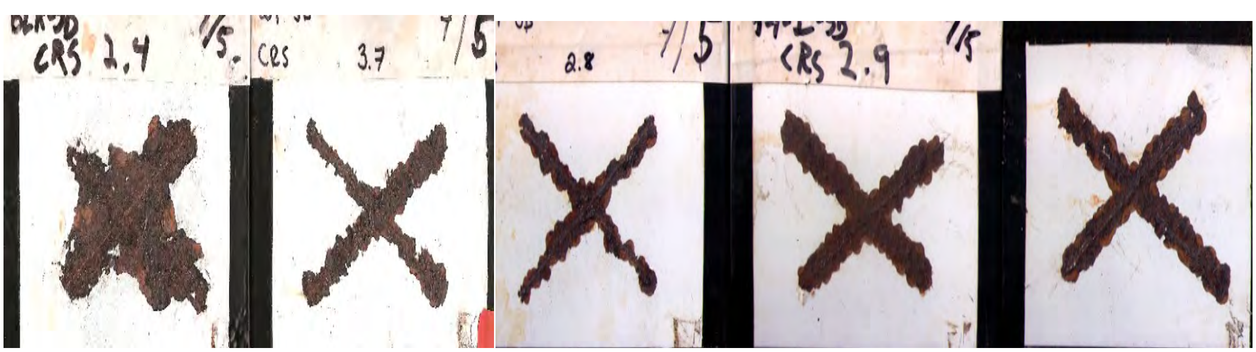
Overall, it seems justified to conclude that for CRS the ECO5-1 systems perform as well as the DoD-P-15328D wash primer in the salt spray test, but generally have better adhesion. The cleaning of the panels prior to ECO5-1 wash primer deposition is not crucial and can, at its simplest, conveniently be performed by sandpaper roughening.

Figures 62 and 63 show the WB- and SB-primed CRS panels after the GM9540P CCT test which was performed for 40 cycles. This test was done with the same panels as those which were examined by EIS, reported in section a). The CCT part of the panels was scribed, the EIS half of each panel was not scribed. The primer thickness was 1.2-2 mil for the WB primer and 2.4-3.7 mil for the SB primer.



(a) (b) (c) (d) (e)

Figure 62. Primed CRS panels after 40 cycles in the GM9540P CCT; the primer was Deft MIL-53030C (WB); (a) untreated control, steel-shot-blasted; (b) DoD-P-15328D wash primer, steel- shot-blasted; (c) ECO5-1 with sandpaper roughening (ECO5-1-1); (d) ECO5-1 on an alkaline-cleaned panel (ECO5-1-2); (e) ECO5-1 on a steel-shot-blasted panel (EC5-1-3).



(a) (b) (c) (d) (e)

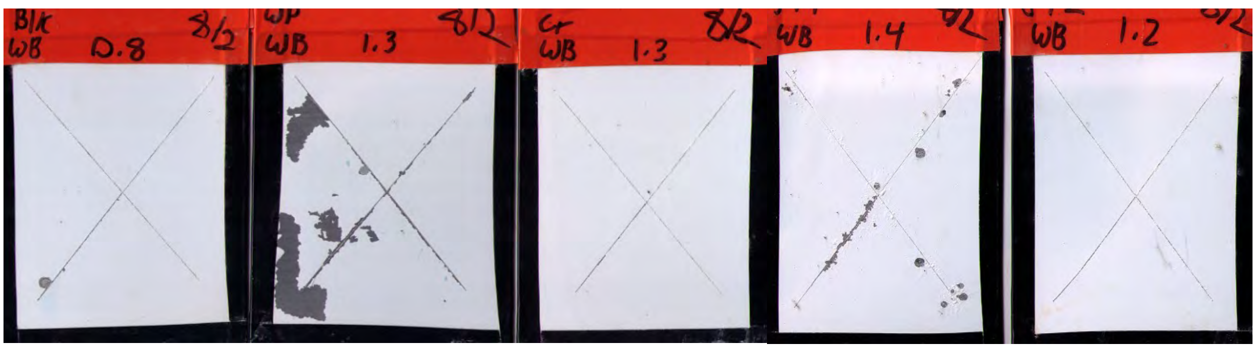
Figure 63. Primed CRS panels after 40 cycles in the GM9540P CCT; the primer was Deft MIL-53022D (SB); (a) untreated control, steel-shot-blasted; (b) DoD-P-15328D wash primer, steel- shot-blasted; (c) ECO5-1 with sandpaper roughening (ECO5-1-1); (d) ECO5-1 on an alkaline-cleaned panel (ECO5-1-2); (e) ECO5-1 on a steel-shot-blasted panel (ECO5-1-3).

These results show that the ECO5-1 performance on CRS is for both primers again very close to

that of the DoD-P-15328D wash primer and better than the untreated panels. For the WB primer (Figure 62) the DoD-P-15328D wash primer may seem to have a little less scribe creep than ECO5-1, but on the other hand the residual adhesion of the ECO5-1 wash primer is better (Table 41). With the SB primer (Figure 63) the scribe creep of DoD-P-15328D and ECO5-1 are identical if one considers the sandpaper roughening cleaning process. Here, too, the residual adhesion of ECO5-1 is better than for the DoD-P-15328D wash primer (Table 41), regardless of the cleaning process used.

With the treated **AA7075-T6** alloy three corrosion tests were performed, the SST, GM9540P and the CASS test. The same Deft WB and SB primers were used as for CRS. Only the metal cleaning methods 1 and 2 were used, as steel shot-blasting is not suited for the thin Al alloy panels. Three controls were used for Al, viz., an untreated sandpaper-roughened panel, the DoD-P-15328D wash primer on a sandpaper-roughened panel and a chromated panel, obtained from ACT Test Panels LLC. The chromating process was Alodine 407.

The SST test panels for the two primers are shown in Figures 64 and 65 and initial adhesion data are presented in Tables 44 and 45.



(a) (b) (c) (d) (e)

Figure 64. Primed AA7075-T6 panels after 500 hours SST; the primer was Deft MIL-53030C (WB); (a) untreated control, sandpaper-roughened; (b) DoD-P-15328D wash primer, sandpaper-roughened; (c) Alodine 407 control; (d) ECO5-1 on a sandpaper-roughened panel (ECO5-1-1); (e) ECO5-1 on an alkaline-cleaned panel (ECO5-1-2).

Table 44. Initial data for WB-primed AA7075-T6 panels shown in Figure 64

Sample ID	DFT (mil)	Dry Adh	Wet Adh
ECO5-1-1*	1.9	5B	5B
ECO5-1-2	1.7	5B	4B
Untreated	1.7	5B	5B
Chromated	2.4	5B	5B
DoD-P-15328D	1.8	5B	0

*Last digit is the metal cleaning process

(a) (b) (c) (d) (e)

Figure 65. Primed AA7075-T6 panels after 500 hours SST; the primer was Deft MIL-53022D (SB); (a) untreated control, sandpaper-roughened; (b) DoD-P-15328D wash primer, sandpaper-roughened; (c) Alodine 407 control; (d) ECO5-1 on a sandpaper-roughened panel (ECO5-1-1); (e) ECO5-1 on an alkaline-cleaned panel (ECO5-1-2).

Table 45. Initial data for SB-primed AA7075-T6 panels shown in Figure 65

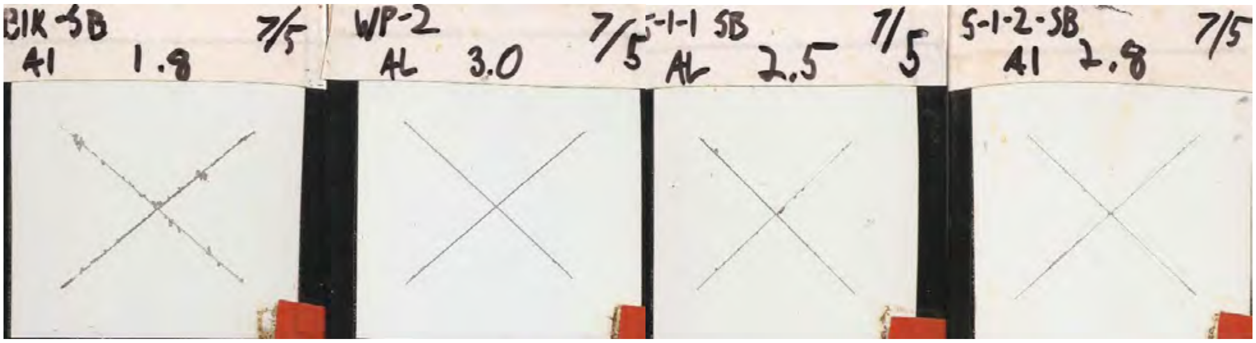
Sample ID	DFT (mil)	Dry Adh	Wet Adh
ECO5-1-1*	1.9	4B	4B
ECO5-1-2	1.8	5B	5B
Untreated	1.8	4B	2B
Chromated	2.1	5B	5B
DoD-P-15328D	1.1	5B	0B

*Last digit is the metal cleaning process

The data demonstrate that the DoD-P-15328D wash primer has a poor wet adhesion to both primers, as had already been concluded earlier on in the project. The two ECO5-1 systems exhibit good dry and wet adhesion to both primers, and so do the chromated panels. The untreated panels adhere well to the WB primer, but less so to the SB primer.

After the SST test there is very little scribe creep, as could be expected, as 500-hour exposure is very short for Al alloys. However, there are blisters along the scribe lines here and there. The DoD-P-15328D wash primer partly delaminates in the tape pull (Figure 64), in agreement with the poor wet adhesion of Table 44. This effect is not seen for the SB primer. The chromated panels are perfect under both primers. Of the ECO5-1 systems, the sandpaper-roughened one seems to be poorer than the alkaline-cleaned panel. The method of cleaning prior to spraying the wash primer on may thus be more important for this alloy than for CRS. The alkaline-cleaned ECO-5-1 performed on par with the chromated panel under the WB primer, but has few small blisters along the scribe line under the SB primer.

Figure 66 shows the AA7075-T6 panels after 80 cycles in the CCT test. Only the SB primer was used here, so only 4 panels are shown. EIS data of the unscribed half of the same panels were presented in Figure 58. The residual adhesion is tabulated in Table 46.



(a) (b) (c) (d)

Figure 66. Primed AA7075-T6 panels after 80 cycles in the GM9540P CCT test; the primer was Deft MIL-53022D (SB); (a) untreated control, alkaline cleaned (BLK); (b) DoD-P-15328D wash primer, alkaline-cleaned (ECO5-1.1); (c) ECO5-1 on a sandpaper-roughened panel; (d) ECO5-1 on an alkaline-cleaned panel (ECO5-1.2).

Table 46. Residual adhesion of panels of Figure 66 after 80 cyles in the GM9540P test

System	Adhesion
AA-BLK-SB	4B
AA-DoD-P-15328D-SB	4B
AA-ECO5-1.1-SB	5B
AA-ECO5-1.2-SB	5B

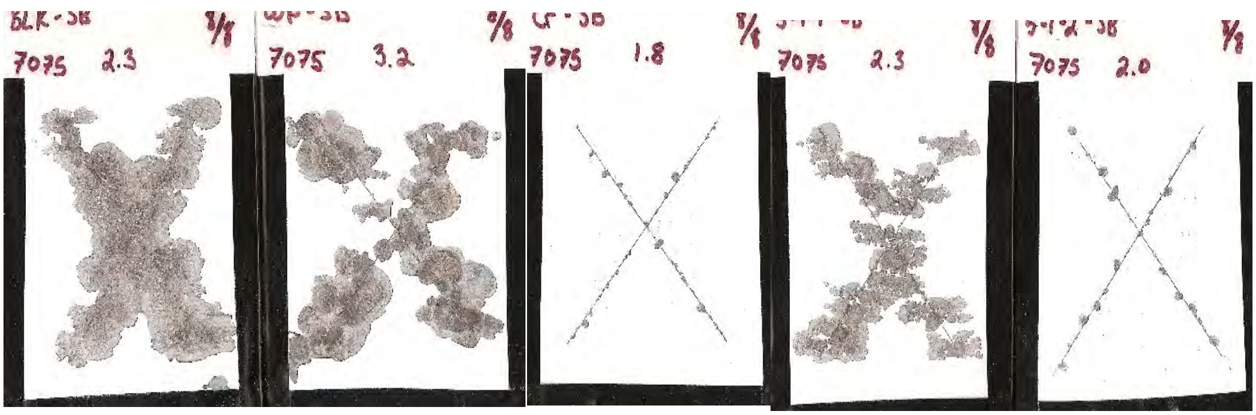
It can be concluded that the two ECO5-1 systems both perform very well in this test. They are at the same level as the DoD-P-15328D wash primer. The only panel with some paint loss is the untreated control. In terms of residual adhesion, we again observe that the ECO5-1 systems perform better than the DoD-15328D wash primer, although the differences are not very pronounced here.

The results of the 240-hour CASS test are shown in Figure 67 and 68. Both primers were tested here and the same wash primers and metal cleaning procedures were applied as in Figures 64 and 65. In this test, as in the other corrosion tests, the entire panel is subjected to a tape pull to remove paint that had come loose during the test for whatever reason.

The first observation here is that the WB primer (Figure 67) has turned blue after the test. This is most likely caused by the presence of the copper in the salt spray solution. The SB primer does not show that effect, illustrating the difference in hydrophilicity between the two primers, as can be expected. The second observation is the high degree of paint loss in some panels and the striking difference between the panels. These effects are almost identical for the two primers used. The third observation is that the chromated panels show the best performance under both primers.

(a) (b) (c) (d) (e)

Figure 67. Primed AA7075-T6 panels after 240 hours CASS; the primer was Deft MIL-53030C (WB); (a) untreated control, sandpaper-roughened; (b) DoD-P-15328D wash primer, sandpaper-roughened; (c) Alodine 407 control; (d) ECO5-1 on a sandpaper-roughened panel; (e) ECO5-1 on an alkaline-cleaned panel.



(a) (b) (c) (d) (e)

Figure 68. Primed AA7075-T6 panels after 240 hours CASS; the primer was Deft MIL-53022D (SB); (a) untreated control, sandpaper-roughened; (b) DoD-P-15328D wash primer, sandpaper-roughened; (c) Alodine 407 control; (d) ECO5-1 on a sandpaper-roughened panel (ECO5-1-1); (e) ECO5-1 on an alkaline-cleaned panel (ECO5-1-2).

Finally, we can conclude that the ECO5-1-2 panels (alkaline-cleaned) perform considerably better than the DoD-P-15328D wash primer, which is only marginally better than the untreated control. The alkaline-cleaned ECO5-1 panel is again better than the sandpaper-roughened one for both primers. Under the SB its performance is identical to that of the chromated panel. It is not clear why the sandpaper-roughened panel lags behind, but one speculation could be the use of acetone for the initial degreasing step of the panel, just before the wash primer deposition. Acetone is not recommended for solvent-cleaning aluminum alloys, as it reacts with the metal, forming a hard-to-remove complex.

Summarizing the outcome of this experiment, there is overwhelming evidence, based on EIS, SST, CCT and CASS tests, that the water-borne, chromate-free and low-VOC ECO5-1 candidate wash primer can safely replace the DoD-P-15328D wash primer on both CRS and AA7075-T6 alloy and for use under either a WB or a SB military primer. The SB primer performs conside-

rably better than the WB primer, especially for CRS, but that difference is an inherent primer property difference and is not affected by the wash primer. There is no loss of performance when switching to the new ECO5-1 wash primer and the adhesion of the new system is better than that of the DoD-P-15328D wash primer. The method of metal cleaning prior to wash primer deposition is not critical and can be as simple as sandpaper roughening for use on CRS. For use on AA7075-T6 an alkaline wash was shown to give better results. A final conclusion is that the CASS test appears to be more suited for testing AA7075-T6 (and other aluminum) panels than either SST or CCT.

B-2. Effect of resin content in ECO5 for AA7075-T6

The EIS results of this experiment have already been reported in Figures 48 and 49 for CRS and AA7075-T6. The objective of the experiment was to optimize the amount of epoxy resin addition to the ECO-008 system. The formulations used were given in Table 21. Initial adhesion data were given in Tables 25 and 26 and performance data for CRS are shown in Figures 13-17 and Table 28. The AA7075-T6 panels were exposed much longer in the CCT test than the CRS panels. They were stopped after 96 cycles. Here the appearance of the panels after the 96-cycle test and the residual adhesion are reported for formulations ECO5-1 and ECO5-2, which differ only in resin content.

Figures 69 and 70 show the scribe region of the EIS/CCT panels for the WB and SB primer, respectively. Table 47 list the residual adhesion measured on the unscribed EIS part of the panels.

(a) (b) (c)

Figure 69. Primed AA7075-T6 panels after 96 cycles in the GM9540P CCT; the primer was MIL-53030C (WB); (a) wash primer formulation ECO5-1 of Table 21; (b) wash primer formulation ECO5-2 of Table 21; (c) DoD-P-15328D wash primer.

(a) (b) (c)

Figure 70. Primed AA7075-T6 panels after 96 cycles in the GM9540P CCT; the primer was MIL-53022D (SB); (a) wash primer formulation ECO5-1 of Table 21; (b) wash primer formulation ECO5-2 of Table 21; (c) DoD-P-15328D wash primer.

Table 47. Adhesion of panels of Figure 69 and 70 after 96 cycles GM9540P

System	Adhesion
AA-ECO5-1-WB	5B
AA-ECO5-2-WB	4B
AA-DoD-P-15328D-WB	0B
AA-ECO5-1-SB	5B
AA-ECO5-2-SB	5B
AA-DoD-P-15328D-SB	5B

The conclusion to be drawn from these data are that under both primers the ECO5 system performs clearly better than the DoD-P-15328D wash primer. The DoD-P-15328D panel of Figure 69 (WB primer) showed, in addition to more paint loss from the scribe region, a considerable number of small blisters which appeared to be filled with corrosion products (difficult to discern in Figure 69c). Such blisters were absent in the ECO5-1 and ECO5-2 panels. The poorer performance of the DoD-15328D wash primer is also seen in the residual adhesion data. Its adhesion to the WB primer has dropped to 0B.

Another conclusion is that there does not seem to be any advantage of increasing the resin level of the ECO5 system higher than that of ECO5-1. This conclusion had already been drawn from the results reported in section 3. Thus the data shown here confirm the selection of ECO5-1 as the proposed replacement of the DoD-P-15328D wash primer.

B-3. Final Comparison of the ECO5-1 system with the DoD-P-15328D wash primer

In this final experiment the work described in Section B-1 was partly repeated for a check of the reproducibility of the new ECO5-1 system. The same metal substrates (CRS and AA7075-T6) primers (WB and SB) and metal cleaning methods (sandpaper roughening, alkaline cleaning and steel-shot basting) were used. The SST and CASS test were not performed, so the data in this experiment consist of EIS, GM9540P CCT and residual adhesion only. The EIS results are shown in Figures 71 and 72.

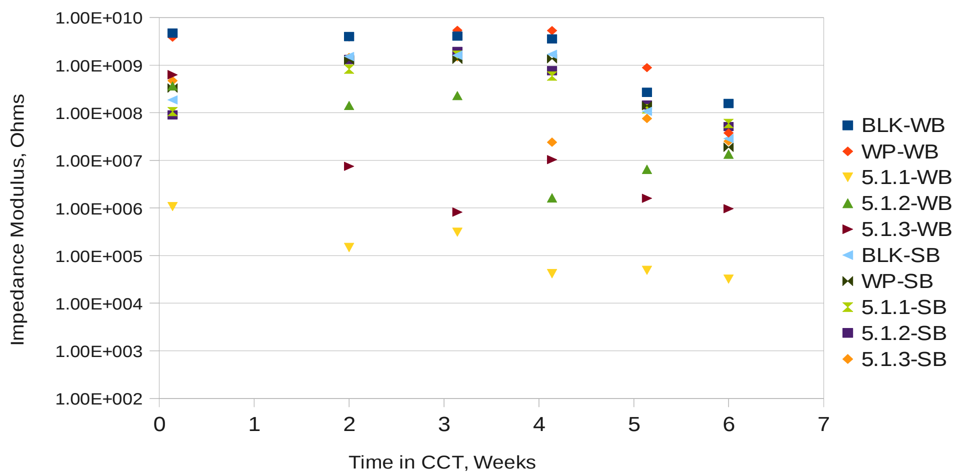


Figure 71. Low-frequency (10^{-2} Hz) modulus vs. 42 cycles exposure time in the CCT GM9540P test of primed CRS; the wash primer was the resin modification 5.1 of Table 21 (ECO5-1) and a commercial wash primer according to DoD-P-15328D; BLK is an untreated control; 5.1.1, 5.1.2 and 5.1.3 are different metal cleaning methods prior to the wash primer application, sandpaper roughening, alkaline cleaning and steel shot-blasting, respectively; the solvent-borne primer was MIL-P-53022D, the water-borne primer was MIL-P-53030C, both from DEFT.

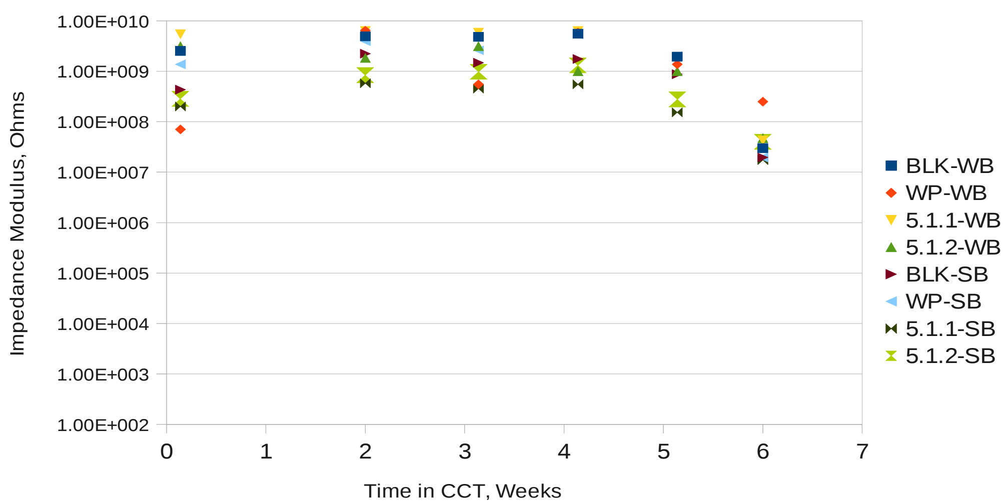


Figure 72. As for Figure 71, but now for AA7075-T6 panels with treatments 1 and 2 only.

For CRS these results are rather puzzling, as none of the 5-1 systems performs well under the

WB primer. They even have a lower impedance than the untreated control (BLK). The performance of these systems in the CCT and adhesion was good, as is shown below. The SB systems behave normally. All systems have a tendency to drop over time, starting at around 4 weeks, which is normal for CRS.

The data for the AA7075-T6 alloy seem normal. All systems are lumped together and also begin to drop slightly after 4 weeks.

The GM9540P test was done for 42 cycles for all metal-primer combinations. It is realized that this exposure time is adequate for CRS but too short for AA7075-T6. However, it was decided to end the test for the AA panels after 42 cycles anyway so that their preliminary results could be included in the final report. The CRS panels after the GM9540P CCT with the loose paint scraped off with a knife, are shown in Figures 73 and 74.

(a) (b) (c) (d) (e)

Figure 73. Primed CRS panels after 42 cycles in the GM9540P CCT; the primer was Deft MIL-53030C (WB); (a) untreated control, steel-shot-blasted; (b) DoD-P-15328D wash primer, steel- shot-blasted; (c) ECO5-1 with sandpaper roughening (ECO5-1.1); (d) ECO5-1 on an alkaline-cleaned panel (ECO5-1.2); (e) ECO5-1 on a steel-shot-blasted panel (EC5-1.3).

(a) (b) (c) (d) (e)

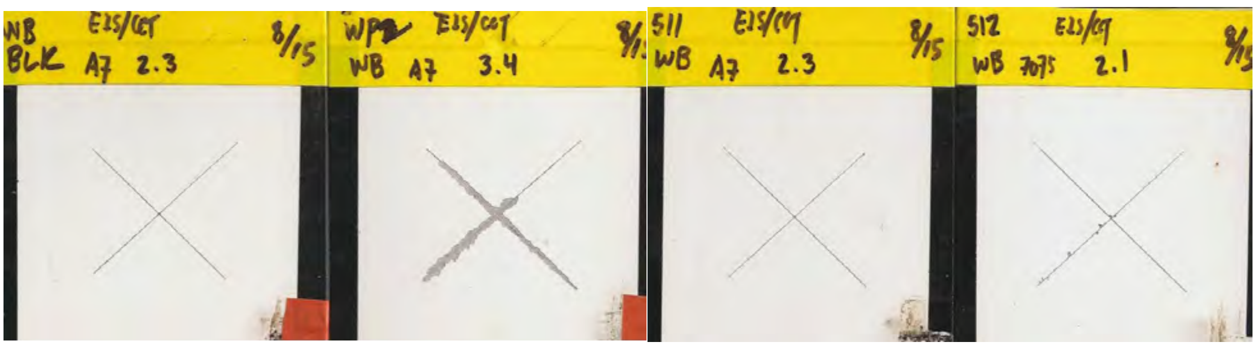
Figure 74. Primed CRS panels after 42 cycles in the GM9540P CCT; the primer was Deft MIL-53022D (SB); (a) untreated control, steel-shot-blasted; (b) DoD-P-15328D wash primer, steel- shot-blasted; (c) ECO5-1 with sandpaper roughening (ECO5-1.1); (d) ECO5-1 on an alkaline-cleaned panel (ECO5-1.2); (e) ECO5-1 on a steel-shot-blasted panel (ECO5-1.3).

When compared with the previous test with the same materials, shown in Figures 62 and 63, it can be concluded that the results are very similar, as can be expected. For both primers the performance of the ECO5-1 systems is very close to that of the DoD-P-15328D wash primer and

all systems perform better than the untreated panel BLK. From Figure 73 (WB primer) it can be seen that the ECO5-1.1 system (sandpaper-roughened) performs slightly better than the DoD-P-15328D wash primer. By and large, the performance of the three ECO5-1 systems is almost the same, so we can again conclude that the type of metal pretreatment prior to wash primer application is not critical.

It can be seen in Figures 73 and 74 (and previous CCT exposures of CRS), that in this test primarily black iron rust is formed. This is Fe_3O_4, rather than the reddish ferric oxide/hydroxide formed in the SST test. The red rust seen bleeding on the panel in Figures 73 c-e, and to a lesser extent in Figures 74 b-e, can be ignored. It is not symptomatic for the ECO5-1 system. It was exclusively formed in the first week of the exposure, when the cure of the room-temperature-cured primer was still incomplete.

The results for the AA7075-T6 panels are shown in Figures 75 and 76.

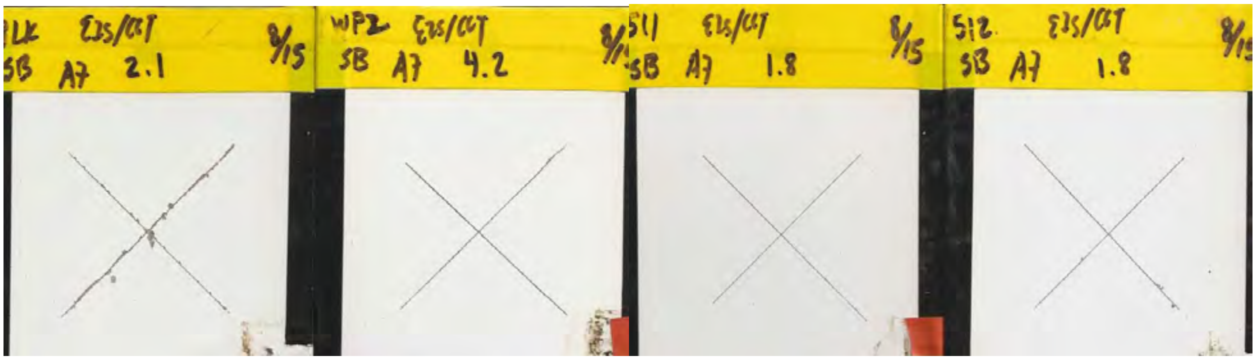


(a) (b) (c) (d)

Figure 75. Primed AA7075-T6 panels after 42 cycles in the GM9540P CCT; the primer was Deft MIL-53030C (WB); (a) untreated control, alkaline-cleaned; (b) DoD-P-15328D wash primer, on an alkaline-cleaned panel; (c) ECO5-1 with sandpaper roughening (ECO5-1.1); (d) ECO5-1 on an alkaline-cleaned panel (ECO5-1.2).

Despite the relatively short exposure time for this metal in the test, some degradation effects can already be noticed. The DoD-P-15328D wash primer does not perform well under the water-borne primer and shows some paint loss along the scribe, in agreement with Figure 69. The other three panels are still in a good state. Under the SB primer (Figure 76), it is the untreated control BLK that has lost some paint along the scribe, similar to the effect shown in Figure 66. The other three panels are still in good shape.

The main conclusions to be drawn from the AA7075-T6 results is that the ECO5-1 system is equivalent to the DoD-P-15328D wash primer when used with the SB primer, but outperforms it when used under the WB primer. The different metal pretreatments prior to ECO5-1 are equivalent between themselves.



(a) (b) (c) (d)

Figure 76. Primed AA7075-T6 panels after 42 cycles in the GM9540P CCT; the primer was Deft MIL-53022D (SB); (a) untreated control, alkaline-cleaned; (b) DoD-P-15328D wash primer, on alkaline-cleaned panel; (c) ECO5-1 with sandpaper roughening (ECO5-1.1); (d) ECO5-1 on an alkaline-cleaned panel (ECO5-1.2).

Table 48. Residual adhesion after the GM9540P test of all panels of Figures 73-76

System	Adhesion
CRS-BLK-WB	1B
CRS-DoD-P-15328D-WB	3B
CRS-ECO5-1.1-WB	5B
CRS-ECO5-1.2-WB	5B
CRS-ECO5-1.3-WB	5B
CRS-BLK-SB	3B
CRS-DoD-P-15328D-SB	4B
CRS-ECO5-1.1-SB	5B
CRS-ECO5-1.2-SB	5B
CRS-ECO5-1.3-SB	5B
AA-BLK-WB	4B
AA-DoD-P-15328D-WB	0B
AA-ECO5-1.1-WB	5B
AA-ECO5-1.2-WB	5B
AA-BLK-SB	0B
AA-DoD-P-15328D-SB	4B
AA-ECO5-1.1-SB	5B
AA-ECO5-1.2-SB	5B

The residual adhesion data for the panels shown in Figures 73-76 are tabulated in Table 48. The data show that the untreated control (BLK) has lost some of its adhesion on both metals and

under both primers, which is not surprising. Remarkable is that the DoD-P-15328D wash primer does not score a 5B in any of the systems. This is in agreement with the adhesion data shown in Tables 41 and 44-47. All ECO5-1 systems score a 5B in all panels. Thus, the overall adhesion of the ECO5-2 replacement wash primer is significantly better than that of the DoD-15328D wash primer. This conclusion is valid for both metal pretreatments tested here, sandpaper-roughening and alkaline cleaning and also for steel-shot-blasting in the case of CRS.

B-4. Conclusions

In summary, the results of section B-1 are confirmed in this experiment. Thus we can conclude that this project has resulted in the development of a wash primer that can replace the DoD-P-15328D wash primer, which was the objective of this project. The wash primer that is proposed is the system ECO5-1. The advantages of this systems are the following.

- It can be applied by spraying using conventional equipment
- The metal pretreatment prior to wash primer application can be alkaline cleaning, cleaning and roughening by sandpaper or steel-shot blasting; the performance on substrates thus treated is approximately the same
- The film formed is thinner, hence the process is economical
- The formulation contains no chromate, very low VOC, no HAPs and no phosphoric acid
- It is water-based, but can be primed in 30 min.; the film dries quickly because of the low film build
- The adhesion to several military WB or SB primers is significantly better than that of the DoD-P-15328D primer; the adhesion remains very good even after exposure in the SST or CCT tests
- The corrosion performance is equal to that of the DoD-P-15328D primer on CRS and better on the aluminum alloy 7075-T6